# Steric Control of Directional Isomerism in Dicopper(I) Helicates of Asymmetrically Substituted 2,2‘:6‘,2‘‘:2‘‘,6‘‘‘-Quaterpyridine Derivatives

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# Steric Control of Directional Isomerism in Dicopper(I) Helicates of Asymmetrically Substituted 2,2′:6′,2″:2″,6‴-Quaterpyridine Derivatives

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**Abstract:** Derivatives of 2,2′:6′,2″:2″,6‴-quaterpyridine have been prepared which are asymmetrically substituted with alkyl groups in the 4- or 6-position and with various substituents in the 4′-position. These ligands form dicopper(I) double helicates which have been investigated by $^{1}$H and $^{13}$C NMR spectroscopic techniques. The formation of helical isomers is shown to depend on the intramolecular interactions between the constituent helicands of the double helicate; 4′-methyl substituents undergo steric interactions with the 4-substituent of the partner helicand, leading to a modest selectivity, although bulky 4-substituents decrease selectivity. In the absence of 4′-substituents, the smaller pitch permits steric interactions between like 4-substituents of the component helicands. In each case, formation of the head-to-head helicate isomer is preferred.

## Introduction

The formation of double-stranded metallosupramolecular helicates from ligands with multiple diimine binding domains and transition metals of various binding geometries has become a classical example of self-assembly in metallosupramolecular systems.[1−7]

The further elaboration of this motif necessitates the introduction of self-organizing elements into the component helicands.[2] This, in turn, depends on mutually interactive functional groups in spatially proximate helicands which can control self-organization through the metal center. One example of this is the selective assembly of helicates from helicands having dissimilar termini, resulting in the formation of one of two possible helicates. In its broadest sense, the self-assembly of directional helicates encompasses the assembly of two dissimilar ligands, akin to the situation found in some dimeric biooligomers, but a more immediate goal is the assembly of two like directional helicand ligands. In this latter case, two possible isomers may be formed. In one, the head-to-head or **HH** isomer, the two like ends lie at the same end of the helicate. In the other, the head-to-tail or **HT** isomer, they lie at opposite ends (see Figure 1). Each of these isomers may exist in enantiomeric **P** or **M** form. The achievement of such directional selectivity could ultimately provide functionalization for the construction of structures having a higher degree of organization, e.g., dimeric and trimeric assemblies of double-helical complexes.

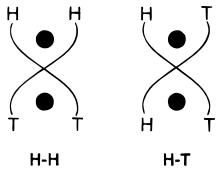


**Figure 1.** Head-to-head and head-to-tail isomers of a dinuclear double helicate.

One approach exploits helicands having metal-binding domains capable of addressing dissimilar metal atoms in an asymmetric fashion.[8−10] Although these studies have been hallmarked by the isolation and characterization of the heterometallic complexes, these substances have only rarely exhibited self-organization.[9] Other investigations have been concerned with helicands bearing symmetrically disposed chiral centers which give helicates dissymmetrical with respect to the mirror plane passing through their midpoints.[11] Inasmuch as these substances give a single helical enantiomer, they are self-organizing, although they are not suitable for investigating directional helication.

Our approach to helical directionality is based on the assembly of double-helical dicopper(I) complexes of asymmetrically substituted 2,2′:6′,2″:2″,6‴-quaterpyridine (qtpy) ligands. The metal atoms in the complexes are approximately tetrahedrally coordinated, and directionality is achieved through steric interactions between alkyl groups on the qtpy skeleton. An

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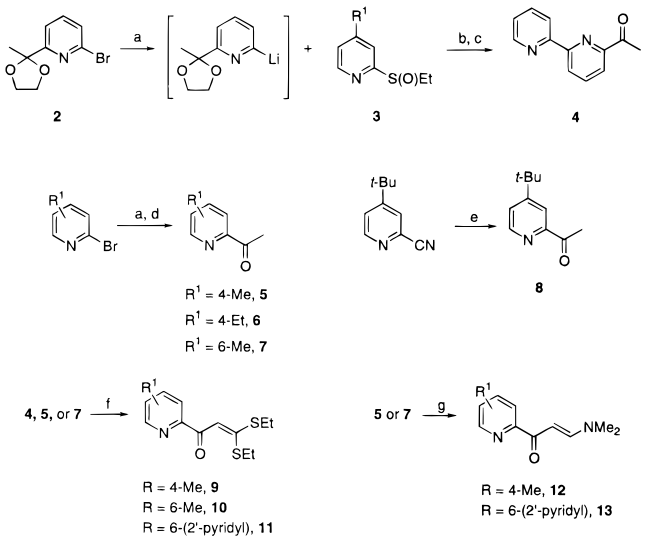
**Scheme 1.** Preparation of Ketone Precursors[a]



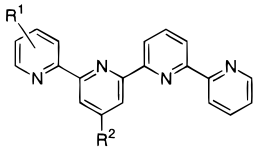

[a] Key: (a) *n*-BuLi, $Et_2O$, −70 °C; (b) THF, →25 °C; (c) 2 M HCl, 60 °C, 2 h; (d) $CH_3C(O)N(CH_3)_2$, →25 °C; (e) MeMgI, $Et_2O$, −15 → +25 °C; (f) 2 KO-*t*-Bu, $CS_2$, 2EtI, THF, 25 °C; (g) $HC(OCH_3)_2N(CH_3)_2$, reflux.

allosteric approach has also been used by others in the preparation of diastereogenic mononuclear[12] and dinuclear[13] metal complexes of diimine ligands. In an earlier paper, we demonstrated that one of the **HH** or **HT** isomers of the double-helical dicopper(I) complex of **1b** is formed in modest excess.[14] In later work, ligand **1c** was shown to unambiguously form exclusively the **HH** helical complex.[15] In this paper, the preparation and characterization of a range of asymetrically-substituted qtpy ligands and their dicopper(I) complexes are described.

## Preparation of Quaterpyridine Ligands

The synthesis of ligands called for the use of 6-acetyl-2,2′-bipyridine (**4**). Although the palladium-catalyzed coupling of 6-bromo-2-acetylpyridine and 2-(trimethylstannyl)pyridine affords this compound in satisfactory yield,[16] the necessity of using fresh tetrakis(triphenylphosphine)palladium and the cost of the associated reagents are disadvantageous. Instead, we have found that the lithiation of 6-bromo-2-(2′-methyl-1′,3′-dioxolan-2′-yl)-pyridine (**2**) followed by nucleophilic addition of the lithio compound to ethyl 2-pyridyl sulfoxide **3** according to the protocol of Oae[17] and acidic hydrolysis afforded **4** in 66% yield (see Scheme 1). The ketones 2-acetyl-4-methylpyridine (**5**) and 2-acetyl-4-ethylpyridine (**6**) were obtained in 37% and 76% yields, respectively, by reaction of *N*,*N*-dimethylacetamide with the corresponding 4-alkyl-2-lithiopyridines. The application of this methodology to the preparation of 2-acetyl-6-methylpyridine (**7**) gave this substance in 24% yield in a mixture of the starting bromide and the desired product. The derivative of this compound used in the appropriate qtpy synthesis could, however, be easily isolated in a pure state (*vide infra*). Treatment of 4-*tert*-butyl-2-cyanopyridine[18] with methylmagnesium iodide afforded 2-acetyl-4-*tert*-butylpyridine (**8**) in 45% yield.

The 4′-(alkylthio)quaterpyridines **1b**−**e** were prepared from these components through cyclization of the thioketene hemiacetals **9**−**11**. These compounds were in turn prepared from the corresponding ketones analogous to Potts's preparation of derivatives of 2-acetylpyridine.[19] Thus, treatment of **4**, **5**, or **7** with carbon disulfide and 2 equiv of ethyl iodide in the presence of 2 equiv of potassium *tert*-butoxide afforded the diethyl thioketene hemiacetals **11**, **9** and **10** in 69%, 81%, and 48% yields, respectively, as pure, crystalline materials. The reaction of ketones **6** and **8** under similar conditions gave oily mixtures of compounds which were not further investigated. The enaminones **12** and **13**, cyclization precursors to the quaterpyridines **1h** and **1i**, were obtained in 61% and 85% yields, respectively, by treatment of the ketones **5** and **7** with excess *N*,*N*-dimethylformamide dimethyl acetal under reflux.[20]



**1**

| | $R^1$ | $R^2$ |
|---|---|---|
| a | 4-H | SMe |
| b | 4-Me | SEt |
| c | 4-Et | SEt |
| d | 4-t-Bu | SEt |
| e | 6-Me | SEt |
| f | 4-Me | $SO_2Et$ |
| g | 4-Me | CN |
| h | 4-Me | H |
| i | 4-t-Bu | H |

Treatment of the pyridine or 2,2′-bipyridine ketones **4**, **6**, and **8** with 2 equiv of potassium *tert*-butoxide followed by the addition of thioketene hemiacetals **9**−**11** or 2-(3′,3′-bis(methylthio)-1′-oxoprop-2′-en-1′-yl)pyridine gave after a variation in the procedure of Potts[19] the alkyl-substituted quaterpyridines **1a**−**e** (see Scheme 2). Similarly, addition of solutions of the enaminones **12** and **13** to solutions of ketones **4** and **8** in the presence of potassium *tert*-butoxide[21] afforded **1h** and **1i**, respectively.

Secondary substituent transformations were demonstrated with qtpy **1b**. Thus, treatment with 2 equiv of *m*-chloroperbenzoic acid gave **1f**. This compound was smoothly converted to **1g** upon heating with an excess of potassium cyanide.[22]

## Quaterpyridine Characterization

All qtpy derivatives were isolated as crystalline materials, although extensive column chromatographic purification of the cyclization products was sometimes required. The purity of these substances is attested to by their analytical data. All showed strong molecular ions in their electron impact mass spectra (EI-MS), the exception being the 4-methyl 4′-ethylsulfonyl derivative **1f** (30% intensity).

The $^1H$ NMR spectra of these compounds reflect their low molecular symmetry (see Table 1). Assignment was made by COSY techniques and by comparison with literature values for

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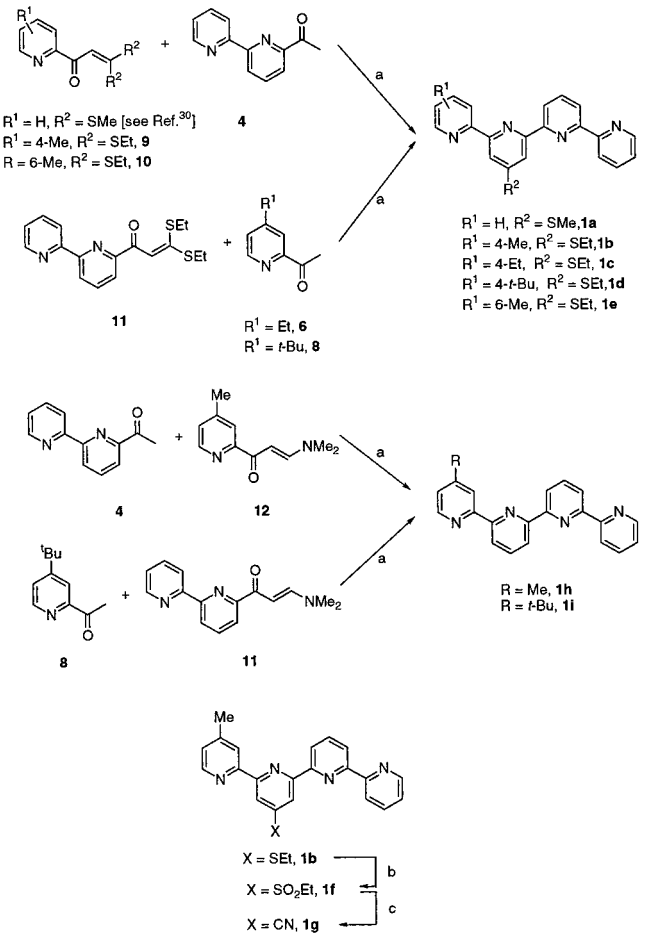
**Scheme 2.** Preparation of Quaterpyridines **1a**−**i**[a]




[a] Key: (a) 2 KO-*t*-Bu, THF, then $NH_4OAc$, AcOH, reflux; (b) 2 equiv of *m*-CPBA, $CH_2Cl_2$, 25 °C, 12 h; (c) KCN, DMF, reflux, 4 d.

qtpy,[23] 4′,4″-bis(methylthio)-qtpy,[19] and various 4′,4″-diaryl-qtpy derivatives.[24] Separate absorptions for all of the protons of the opposing terminal and internal pyridine rings are observed, the exception being compounds **1d** and **1i**, for which overlap of H-5/5-5‴ and H-6/H-6‴ occurs.

The 4′-alkylthio derivatives **1a**−**d** exhibit similar absorption patterns in the aromatic regions (see Figure 2). The signals from given protons of the second, third, and fourth pyridine rings occur at virtually identical shift values in each case. Those from the alkyl-substituted rings, in particular H-3 and H-6, show minor shift differences which can be attributed to the type of alkyl substitution in the particular compound. The coupling constants $^3J_{H,H}$ are in the 7−8 Hz range, the exception being those for the H-5−H-6 and H-5‴−H-6‴ systems, which lie between 4 and 5 Hz. The coupling constant $^4J_{H,H}$ was observed to be 1.7−1.8 Hz in all cases. These hallmarks are also exhibited in the spectra of the derivatives **1f** and **1g**, the only major differences being attributed to the presence of the electron-withdrawing groups in the 4′-position, which results in a strong downfield shifting of the signals from H-3′ and H-5′.

The spectra of the 4-monosubstituted derivatives **1h** and **1i** are significantly more complicated, although COSY techniques allow identification of many absorptions. In particular, the resonances of H-3 and H-6 on both terminal pyridine rings can be discerned. Interestingly, of all of the qtpy derivatives investigated, **1i** alone shows $\delta^{H3} > \delta^{H6}$. Overall, however, this

**Table 1.** $^1$H NMR Spectroscopic Shifts [$\delta$] and Coupling Constants [$^3J$, $^4J$, Hz] for Quaterpyridine Ligands in $CDCl_3$ Solution (300 MHz)

| | **1a** | **1b**[a] | **1c** | **1d** | **1e** | **1f** | **1g** | **1h** | **1i** |
|---|---|---|---|---|---|---|---|---|---|
| H-3 | 8.62−8.66[b] | 8.43 | 8.46 | 8.61 | 8.42 [$^3J$, 7.8] | 8.46 | 8.36 | 8.45−8.50[b] | 8.63−8.67[b] |
| H-4 | 7.84−7.92[b] | | | | 7.72 [$^3J$ 7.6] | | | | |
| H-5 | 7.26−7.37[b] | 7.15 [$^3J \approx 1$] | 7.19 [$^4J$, $^3J$ 1.8, 5.0] | 7.31−7.36[b] | 7.20 [$^3J$ 7.8] | 7.23 [$^3J$ 4.5] | 7.19 [$^3J \approx 5.0$] | 7.17 [$^4J$, $^3J$ 0.9, 5.0] | 7.29−7.34[b] |
| H-6 | 8.69−8.73[b] | 8.53 [$^3J$ 5.2] | 8.58 [$^3J$ 4.3] | 8.52 [$^4J$ 1.8] | 8.50 [$^4J$ 1.7] | 8.60 [$^3J$ 4.9] | 8.53−8.58[b] | 8.57 [$^3J$ 4.7] | 8.61 [$^3J$ 5.2] |
| H-3′ | 8.51 [$^4J$ 1.8] | 8.49 [$^4J$ 1.8] | 8.51 [$^4J$ 1.8] | 8.52 [$^4J$ 1.8] | 8.50 [$^4J$ 1.7] | 9.07 [$^4J$ 1.4][c] | 8.75[c] | 8.65−8.70[b] | 8.63−8.67[b] |
| H-4′ | | | | | | | | 8.02 [$^3J$ 7.8][c] | 8.00 [$^3J$ 8.4][c] |
| H-5′ | 8.34 [$^4J$ 1.8] | 8.33 [$^4J$ 1.8] | 8.34 [$^4J$ 1.8] | 8.34 [$^4J$ 1.8] | 8.37 [$^4J$ 1.7] | 8.95 [$^4J$ 1.8][c] | 8.64[c] | 8.65−8.70[b] | 8.63−8.67[b] |
| H-3″ | 8.62−8.66[b,c] | 8.63 [$^3J$ 7][c] | 8.64 [$^4J$, $^3J$ 1.0, 7.8][c] | 8.61 [$^4J$, $^3J$ 1.6][c] | 8.64 [$^4J$, $^3J$ 1.5, 7.8][c] | 8.65−8.72[b,c] | 8.53−8.58[b,c] | 8.45−8.50[b] | 8.44−8.49[b] |
| H-4″ | 7.99 [$^3J$ 7.9] | 8.00 [$^3J$ 7.8] | 8.00 [$^3J$ 7.8] | 8.00 [$^3J$, 7.8] | 7.98 [$^3J$ 7.8] | 8.05 [$^3J$ 7.8] | 7.99 [$^3J$ 7.8] | 7.99 [$^3J$ 7.8][c] | 7.97 [$^3J$ 8.3][c] |
| H-5″ | 8.48 [$^4J$, $^3J$ 1.0, 7.8][c] | 8.47 [$^3J$ 8][c] | 8.48 [$^4J$, $^3J$ 1.1, 7.8][c] | 8.48 [$^4J$, $^3J$ 1.0, 7.8][c] | 8.47 [$^4J$, $^3J$ 0.9, 7.9][c] | 8.57 [$^3J$ 7.8][c] | 8.51 [$^3J$ 7.9][c] | 8.45−8.50[b] | 8.44−8.49[b] |
| H-3‴ | 8.62−8.66[b] | 8.61 [$^3J$ 7] | 8.63 [$^4J$, $^3J$ 1.0, 7.9] | 8.64−8.65[b] | 8.63 [$^4J$, $^3J$ 1.0, 7.9] | 8.65−8.72[b] | 8.53−8.58[b] | 8.65−8.70[b] | 8.63−8.67[b] |
| H-4‴ | 7.84−7.92[b] | 7.89 [$^4J$, $^3J$ 1.8, 7.7] | 7.88 [$^4J$, $^3J$ 1.8, 7.6] | 7.88 [$^4J$, $^3J$ 1.8, 7.8] | 7.89 [$^4J$, $^3J$ 1.7, 7.8] | 7.91 [$^4J$, $^3J$ 1.5, 7.8] | 7.88 [$^4J$, $^3J$ 1.7, 7.7] | 7.88 [$^4J$, $^3J$ 1.8, 7.7] | 7.84 [$^4J$, $^3J$ 1.6, 7.7] |
| H-5‴ | 7.26−7.37[b] | 7.35 [$^4J$, $^3J$ 1.2, 4.8, 7.4] | 7.34 [$^4J$, $^3J$, $^3J$ 1.2, 4.8, 7.5] | 7.31−7.36[b] | 7.35 [$^4J$, $^3J$ 1.2, 4.6, 7.5] | 7.37 [$^3J$, $^3J$ 4.8, 6.7] | 7.34 [$^3J$, $^3J$ 4.8, 7.4] | 7.35 [$^4J$, $^3J$, $^3J$ 1.2, 4.8, 7.5] | 7.29−7.34[b] |
| H-6‴ | 8.69−8.73[b] | 8.71 [$^3J$, $^4J$ 0.9, 4.8] | 8.71 [$^3J$, $^4J$ 0.9, 4.8] | 8.71 [$^3J \sim 4$] | 8.71 [$^3J \approx 5$] | 8.65−8.72[b] | 8.69 [$^4J$, $^3J$ 0.8, 4.0] | 8.72 [$^4J$, $^3J$ 1.8, 4.8] | 8.70 [$^3J \approx 5$] |
| other | 2.71 [$SCH_3$] | 3.22 [$^3J$ 7.3 Hz, $SCH_2$], 2.48 [$CH_3$], 1.48 [$^3J$ 7.3, $SCH_2CH_3$] | 3.24 [$^3J$ 7.4, $SCH_2$], 2.80 [$^3J$ 7.6, $CH_2$)], 1.49 [$^3J$ 7.4, $SCH_2CH_3$], 1.36 [$^3J$ 7.6, $CH_2CH_3$] | 3.24 [$^3J$ 7.4, $SCH_2$], 1.49 [$^3J$ 7.4, $SCH_2CH_3$], 1.44 [s, $C(CH_3)_3$] | 3.24 [$^3J$ 7.3, $SCH_2$], 2.66 [$CH_3$], 1.50 [$^3J$ 7.3, $SCH_2CH_3$] | 3.32 [$^3J$ 7.4, $SO_2CH_2$], 2.53 [$CH_3$], 1.41 [$^3J$ 7.4, $SO_2CH_2CH_3$] | 2.50 [$CH_3$] | 2.52 [$CH_3$] | 1.43 [$C(CH_3)_3$] |

[a] Taken from ref 14. [b] Multiplet; [c] Opposite assignment equally possible.

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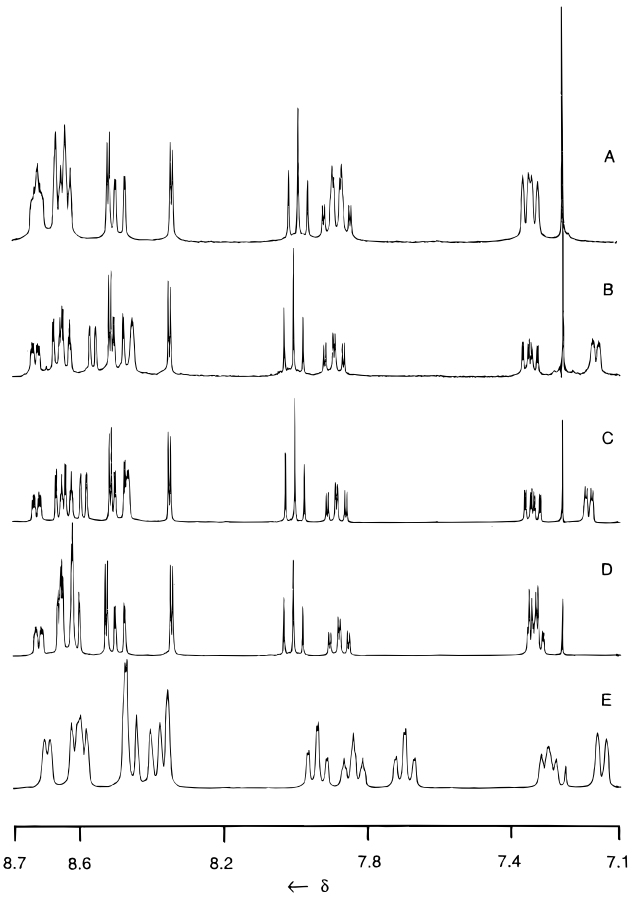



**Figure 2.** Partial $^1$H NMR spectra of qtpy derivatives in $CDCl_3$ solution (300 MHz): (A) **1a**; (B) **1b**; (C) **1c**; (D) **1d**; (E) **1e**.

finding agrees with the changes in chemical shift according to alkyl substitution observed for the 4-alkyl-4′-(alkylthio)-quaterpyridines.

The signals from the side chain substituents of **1a**−**e** occur within the expected values on the basis of comparison to literature values;[19] the resonances of the ethyl groups of **1c** were further distinguished from each other through NOESY spectra. No other significant through-space coupling between alkyl and aromatic positions was observed for any of the compounds.

### Crystal Structures of 4-Methyl-4′-(ethylthio)-2,2′:6′,2″:2″,6‴-quaterpyridine (1b) and 4-Methyl-2,2′:6′,2″:2″,6‴-quaterpyridine (1h)

Compounds **1b** and **1h** were further characterized through crystal structures (see Figures 3 and 4). The pyridine rings in both ligands adopt the expected *trans*,*trans*,*trans*-conformation in the solid state, and all bond lengths and angles are within expected limits. Although the adjacent pyridine rings of both are essentially coplanar, the angles between the mean planes of the two terminal pyridine rings are 8.6° for **1b** and 2.7° for **1h**, and thus these molecules are slightly riffled in the solid state. The torsion angles between the two bipyridine halves are 3.5° (**1b**) and 2.5° (**1h**). The S−C−C framework of the ethylthio residue in **1b** is essentially coplanar with its adjoining pyridine ring. The geometry of the qtpy cores of both thus closely resemble that of qtpy.[25]

Compound **1b** crystallizes in the $P\bar{1}$ space group (see Figure 5 and Table 2); adjacent pairs of **1b** molecules occur around an inversion center with close contacts of 3.5−3.8 Å between the mean qtpy planes. The next nearest pairs of molecules also exhibit moderate overlap of the opposing terminal pyridine rings (closest interplanar distances ∼3.5 Å). Compound **1h** crystallizes in the $P2_1/n$ space group (see Figure 6). The molecules adopt a herringbone array in the solid state, with closest pairs being related through an inversion center. The stacking contacts to the next closest molecules are between substituted and unsubstituted terminal pyridine rings (interplanar distances ∼3.5 Å).

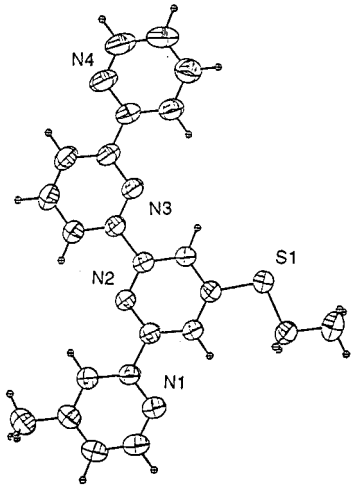



**Figure 3.** Solid state structure of 4-methyl-4′-(ethylthio)-6′:2′,6″;2″,6‴-quaterpyridine (**1b**).

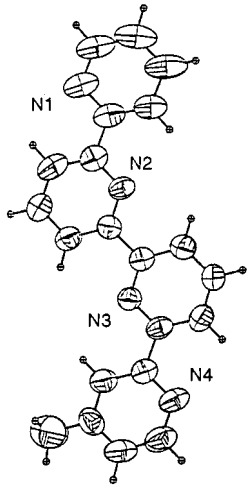



**Figure 4.** Solid state structure of 4-methyl-2,6′:2′,6″;2″,6‴-quaterpyridine (**1h**).

### Preparation of Dicopper(I) Helicates

The dicopper(I) helicates were prepared by heating degassed methanolic mixtures of the appropriate ligand and 1 equiv of tetrakis(acetonitrile)copper(I) hexafluorophosphate for 30−60 min, precipitated by the addition of a large excess of methanolic ammonium hexafluorophosphate, and recrystallized by slow diffusion of diethyl ether or diisopropyl ether vapor into acetonitrile solutions (see Scheme 3). The dinuclear nature of the copper(I) complexes is apparent from their mass spectra and is in accord with previous findings.[1,23,26] The $^1$H NMR spectra of the complexes are characterized by sharp signals. While all of the complexes are stable in the solid state, the complex $[Cu_2(\mathbf{1d})_2][PF_6]_2$ was oxidized slowly in solution to a mononuclear copper(II) complex. Upon attempted recrystallization of the complex $[Cu_2(\mathbf{1g})_2][PF_6]_2$, substantial decomposition to give other copper(I) compounds, which were not further investigated, occurred.

(25) Constable, E. C.; Elder, S. M.; Healy, J.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1990**, 1669−1674.
(26) Constable, E. C.; Hannon, M. J.; Martin, A.; Raithby, P. R.; Tocher, D. A. *Polyhedron* **1992**, *11*, 2967−2971.

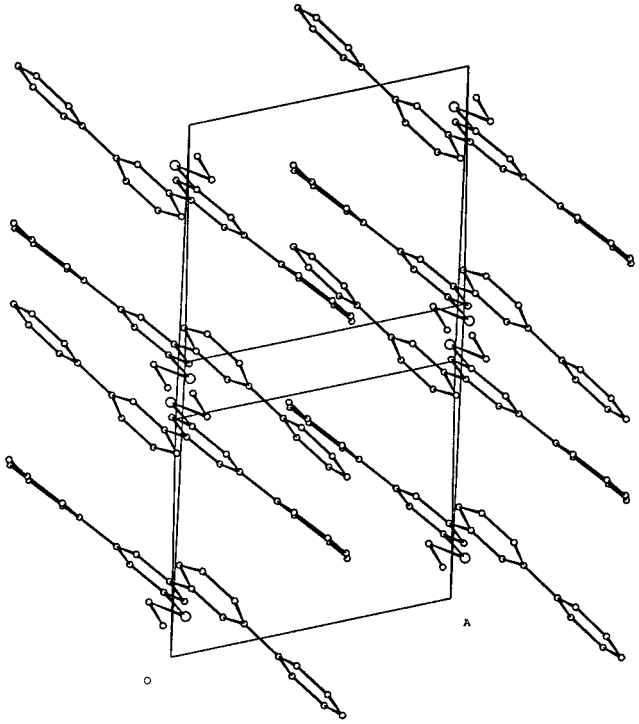


**Figure 5.** Packing of 4-methyl-4′-(ethylthio)-6′:2′,6″;2″,6‴-quaterpyridine (**1b**) in the crystal lattice.

**Table 2.** Crystal Data and Parameters of Data Collection for **1b** and **1h**

| | **1b** | **1h** |
|---|---|---|
| formula | $C_{23}H_{20}N_4S$ | $C_{21}H_{16}N_4$ |
| mol. weight | 384.498 | 324.387 |
| crystal system | triclinic | monoclinic |
| spacegroup | $P\bar{1}$ | $P2_1/n$ |
| $a$ (Å) | 9.114(1) | 11.544(1) |
| $b$ (Å) | 10.790(1) | 12.399(2) |
| $c$ (Å) | 10.954(1) | 12.625(1) |
| α (deg) | 78.565(6) | 90.000 |
| $\beta$ (deg) | 71.759(7) | 111.235(8) |
| $\gamma$ (deg) | 89.497(5) | 90.000 |
| volume (Å$^3$) | 1001.18(2) | 1684.4(3) |
| $Z$ | 2 | 4 |
| $F$(000) | 404 | 680 |
| density (g cm$^{-3}$) | 1.275 | 1.279 |
| $\mu$ (cm$^{-1}$) | 15.06 | 5.80 |
| crystal size (mm) | 0.08 × 0.24 × 0.28 | 0.30 × 0.45 × 0.65 |
| temperature (K) | 293 | 293 |
| radiation | Cu Kα ($\lambda$ = 1.541 80) | Cu Kα ($\lambda$ = 1.541 80) |
| scan type | $\omega-2\theta$ scans | $\omega-2\theta$ scans |
| $\theta_{max}$ (deg) | 74.33 | 77.50 |
| no. of measured reflns | 4359 | 3894 |
| no. of independent reflns | 4090 | 3342 |
| no. of reflns in refinement | 2552 | 1415 |
| no. of variables | 253 | 227 |
| final $R$ | 0.0774 | 0.0804 |
| final $R_w$ | 0.0870 | 0.0570 |
| last max/min in difference map | 0.540/−0.453 | 0.644/−0.244 |

The evaluation of the **HH**:**HT** ratios for these complexes and the assignment of spectroscopic and physical properties to the individual isomers were of central interest to this work. The isomeric **HH**−**HT** pairs coelute in all of the chromatographic systems which we have investigated, and in the absence of a strong preference for a given isomer, X-ray crystallographic analysis is unlikely to be definitive. We have, thus, relied principally on $^1$H NMR spectroscopic techniques to distinguish between the isomers and to establish the isomeric ratios. The signs and magnitudes of the changes in aromatic chemical shifts upon helicate formation with copper(I) agree with those observed for qtpy[23,25] and 4′,4″-bis(methylthio)-2,2′:6′,2″:6″,2‴-quaterpyridine,[19] although the aromatic regions are notably more complicated.

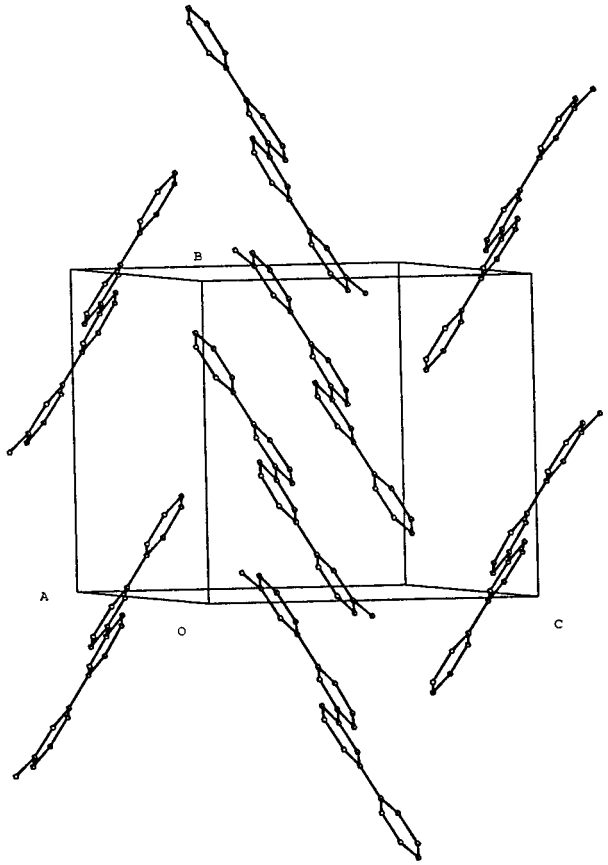
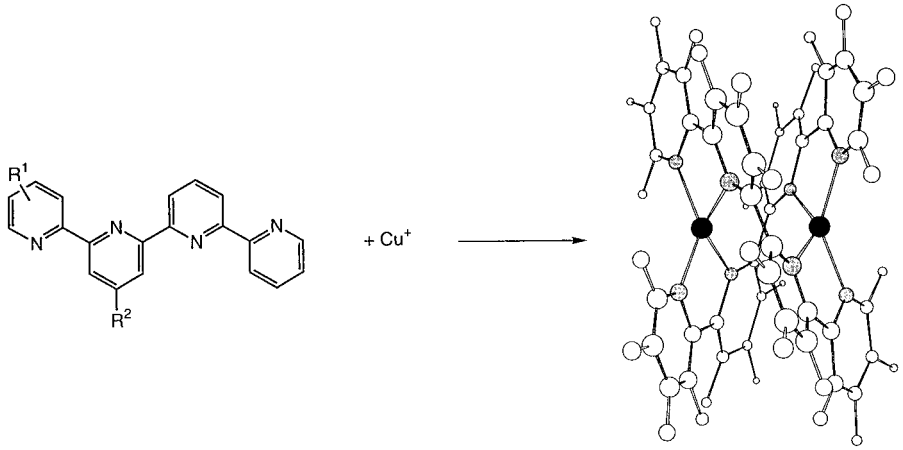


**Figure 6.** Packing of 4-methyl-2,6′:2′,6″;2″,6‴-quaterpyridine (**1h**) in the crystal lattice.

In the complex $[Cu_2(\mathbf{1a})_2][PF_6]_2$, the resonances of H-5 and H-5‴ at $\delta$ 7.35 are split into two multiplets at $\delta$ 7.24−7.38 (see Figure 7). Because of the equal integral intensity and form of these signals, we assign them to *pairs* of H-5 and H-5‴ from **HH** and **HT** (or *vice versa*) isomers. The signals from H-3′ and H-5′ appear as four doublets ($^4J \approx 1.7$ Hz) at $\delta$ 7.46−7.65 of similar intensity. All other signals in the aromatic region appear downfield in a multiplet at $\delta$ 7.76−8.08 comparable to those observed for $[Cu_2(qtpy)_2][PF_6]_2$.[23,26] The methylthio group is observed as two singlets of equal intensity at $\delta$ 2.60 and 2.61. Accordingly, we conclude that a 1:1 mixture of **HH** and **HT** isomers is formed with **1a**.

In the complex $[Cu_2(\mathbf{1b})_2][PF_6]_2$, the shifts of H-5 and H-5‴ are observed as two doublets at $\delta$ 7.07/7.17 ($^3J = 4$ Hz) and two multiplets at $\delta$ 7.06−7.36, each signal pair of like multiplicity integrating in a ratio of 3:2. The signals of H-5 in the minor and major isomers are observed through COSY techniques to couple with protons H-6 at $\delta$ 7.73 and 7.77, respectively, with $^3J \approx 4$ Hz. The signals from H-3′ and H-5′ appear as four doublets ($^3J \approx 1$ Hz) at $\delta$ 7.44, 7.53, 7.55, and 7.64. Here, the integral intensities are the same for the first and the fourth and for the second and third signals, and the ratio of integral intensities between these two signal pairs is also 3:2. Thus, each pair of integral-matched signals arises from H-5, H-3′, H-5′, and H-5‴ of the same isomer. These ratios are also observed when the complex is prepared from the ligand and $[Cu(CH_3CN)_4][PF_6]$ in benzene. For H-5, H-5‴, and the 4-methyl group, the 3:2 ratio does not alter in the temperature range between −20 and +25 °C, while for H-3′ and H-5′, signal overlap occurs with decreasing temperature. In the $^1$H NMR

**Scheme 3.** Preparation of Dicopper(I) Helicates




spectrum of $[Cu_2(\mathbf{1b})_2][PF_6]_2$ in $(CD_3)_2SO$, the paired resonances of the 4-methyl group and of H-5 and H-5‴ are observed at $\delta$ 2.44/2.49, 7.14/7.22, and 7.29−7.33/7.36−7.40, respectively. The intensities of all these signals also integrate in a 3:2 ratio. All of these assignments are in quantitative agreement with an **HH**:**HT** ratio on the basis of the integral intensities from the signals of the 4-methyl group at $\delta$ 2.45 and 2.50 in $CD_3CN$. Similarly, the $^1$H NMR spectra of the complexes $[Cu_2(\mathbf{1f})_2][PF_6]_2$ and $[Cu_2(\mathbf{1g})_2][PF_6]_2$ exhibit methyl resonances at $\delta$ 2.48/2.50 and 2.47/2.55, respectively, in a 3:2 ratio, the downfield resonance being of greater intensity for both.

Thus, a 3:2 preference in favor of one isomer is apparent for all three helicates. As the unlike integration patterns were invariant when the $^1$H NMR spectrum of $[Cu_2(\mathbf{1b})_2][PF_6]_2$ was recorded with various relaxation delays, we are certain that they do not arise from relaxation phenomena.

The complex $[Cu_2(\mathbf{1e})_2][PF_6]_2$ exhibits similar trends in aromatic chemical shifts. In particular, a broad multiplet at $\delta$ 7.24−7.41 for H-5 and H-5‴ and four doublets at $\delta$ 7.33, 7.39, 7.53, and 7.64 are observed, which can be assigned to H-3′ and H-5′. Here, pronounced signal overlap precludes the reliable evaluation of the isomeric ratio. However, the 6-methyl group is observed as two singlets at $\delta$ 2.15/2.16 with an integral ratio of 3:2. Again, this ratio remained unchanged in the two singlets at $\delta$ 1.80/1.91 in $(CD_3)_2SO$.

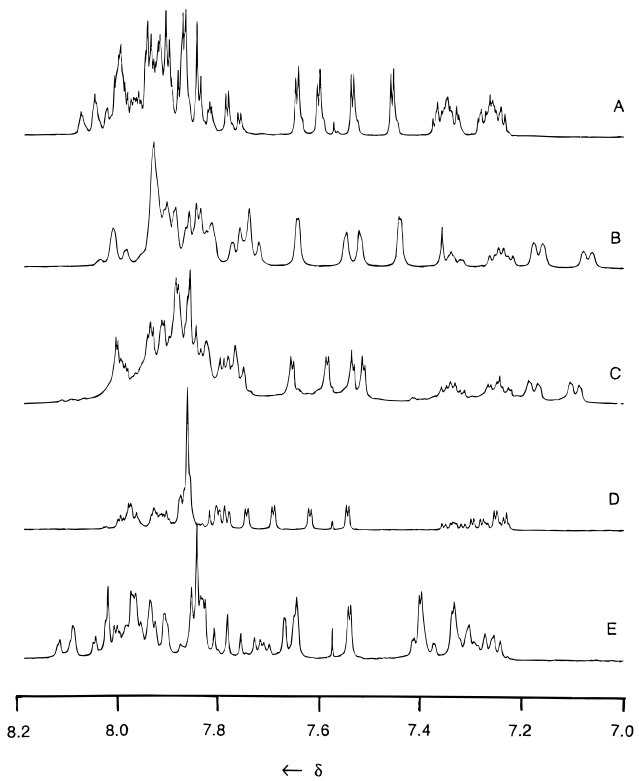



**Figure 7.** Partial $^1$H NMR spectra of the dinuclear double helicates in $CD_3CN$ solution (300 MHz): (A) $[Cu_2(\mathbf{1a})_2][PF_6]_2$; (B) $[Cu_2(\mathbf{1b})_2][PF_6]_2$; (C) $[Cu_2(\mathbf{1c})_2][PF_6]_2$; (D) $[Cu_2(\mathbf{1d})_2][PF_6]_2$; (E) $[Cu_2(\mathbf{1e})_2][PF_6]_2$.

The aromatic regions of the $^1$H NMR spectra of the complexes $[Cu_2(\mathbf{1c})_2][PF_6]_2$ and $[Cu_2(\mathbf{1d})_2][PF_6]_2$ exhibit qualitatively similar results. In $[Cu_2(\mathbf{1c})_2][PF_6]_2$, the signals of H-5 and H-5‴ are observed as two doublets and two multiplets at $\delta$ 7.10/7.18 and 7.23−7.36, of equal intensity, while in $[Cu_2(\mathbf{1d})_2][PF_6]_2$ these resonances overlap. The resonances of H-3′ and H-5′ occur as four doublets ($^3J \approx 1.6$ Hz) at $\delta$ 7.52−7.66 and 7.55−7.74, respectively. In the alkyl region, signal overlap between the different isomers and substituents is observed. Evaluation of the isomeric ratios for $[Cu_2(\mathbf{1c})_2][PF_6]_2$ was possible from either H-5/H-5‴ or H-3′/H-5′, while for $[Cu_2(\mathbf{1d})_2][PF_6]_2$, the latter signal grouping was used. For both complexes, a 1:1 ratio of isomers was found. When present, the resonances of the ethylthio substituents appear as either multiplets or broad triplets at $\delta$ ∼1.42−1.46 and broad quartets at $\delta$ ∼3.07−3.20.

The $^{13}$C NMR spectra of complexes $[Cu_2(\mathbf{1b})_2][PF_6]_2$ and $[Cu_2(\mathbf{1e})_2][PF_6]_2$ have been measured in $(CD_3)_2SO$ at 75 MHz (see Figure 8). In the alkyl region, resonances are observed at $\delta$ 24.2, 20.7/20.9, and 13.4/13.5. Measured in 70% $(CD_3)_2SO$−30% $CDCl_3$, the ligand **1b** exhibited signals at $\delta$ 24.3, 20.7, and 13.3, and we assign the resonances at $\delta$ 24.2, 20.7/20.9, and 13.4/13.5 to the 4′-$SCH_2\mathit{CH}_3$, 4-$\mathit{CH}_3$, and 4′-$S\mathit{CH}_2CH_3$ carbon atoms. Likewise for $[Cu_2(\mathbf{1e})_2][PF_6]_2$, signals were observed at $\delta$ 24.8/24.6, 24.1, and 13.4, which were assigned by APT techniques to the 6-$\mathit{CH}_3$, 4′-$S\mathit{CH}_2CH_3$, and 4′-$SCH_2\mathit{CH}_3$ groups. The splitting of the signals for the isomers is more pronounced for those atoms closest to the helical core of the complexes.

## Discussion

It was initially anticipated that a systematic increase of bulk in the 4-position in the ligand series **1a**−**d** would, on the basis of steric interactions with the 4′-substituent of the partner helicand, result in an increasing preference for the formation of the **HH** over the **HT** isomer. Although the dicopper(I) helicates from **1b** (and **1e**) exhibit a 3:2 preference for one of their isomers, no selectivity is observed with the more sterically demanding compounds **1c** and **1d** nor with **1a**. Thus, the presence of a 4′-alkylthio group either activates or deactivates the helicate to directional selectivity. On the other hand, **1i** forms exclusively the **HH** helicate isomer, while **1h** gives equal amounts of **HH** and **HT** isomers.[15] It therefore appears that

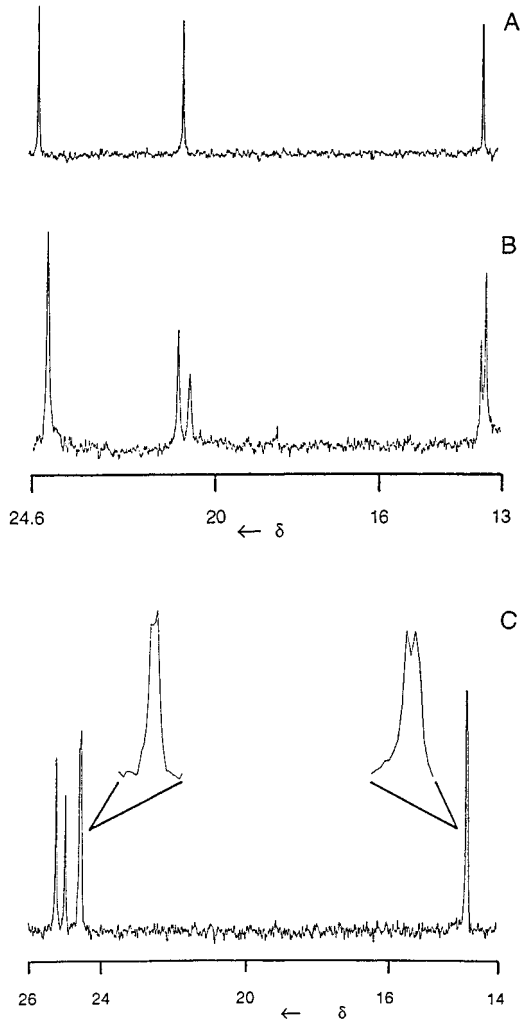



**Figure 8.** Partial $^{13}C$ NMR spectra (75 MHz): (A) ligand **1b** in 70% $(CD_3)_2SO$−30% $CDCl_3$; (B) $[Cu_2(\mathbf{1b})_2][PF_6]_2$ in $(CD_3)_2SO$; (C) $[Cu_2(\mathbf{1e})_2][PF_6]_2$ in $(CD_3)_2SO$.

several different modes of steric interaction together determine the observed directional selectivity.

From computer-based modeling studies[27] on the dicopper(I) qtpy helicate, it is found that steric interactions between the 4-alkyl substituent of one helicand and the 4′-alkylthio group of the partner helicand lead to the mild preference for the **HH** isomer of $[Cu_2(\mathbf{1b})_2][PF_6]_2$. However, the lack of directional selectivity in the complexes from ligands **1c** and **1d** implicates the absence of such interactions. The sensitivity of the helical bite to substitution has been documented for other qtpy helicates,[3,7,23] and steric repulsion in these complexes might thereby be relieved through a buttressing effect, which increases the dihedral angle between the individual 2,2′-bipyridine units of each component helicand and thereby increases the separation between the substituent pair (see Figure 9A,B).

In the absence of a 4′-substituent, the helix is shorter, giving rise to the situation found in the helicates $[Cu_2(\mathbf{1h})_2][PF_6]_2$ and $[Cu_2(\mathbf{1i})_2][PF_6]_2$. In the case of $[Cu_2(\mathbf{1h})_2][PF_6]_2$, no interhelicand/intrahelicate interactions exist, and no selectivity is possible. For $[Cu_2(\mathbf{1i})_2][PF_6]_2$, however, the steric interactions between the *tert*-butyl groups of a **HT** isomer cause it to be disfavored relative to the **HH** isomer (see Figure 9C).

The changes in helical pitch with the 4-alkyl-4′-alkylthio)-qtpy helicates alters the degree of $\pi$-stacking possible in the helical complexes. In turn, the extent of $\pi$-stacking is reflected

(27) *Chem3D/Version 3.1.1*; Cambridge Scientific Computing: Cambridge, MA, 1992.

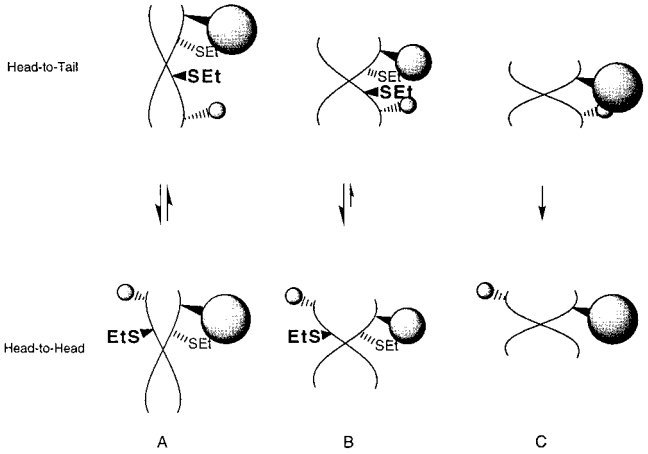



**Figure 9.** Interstrand interaction of 4-substituents in dimeric helicates: (A) extended helicate with noninteracting substituents; (B) intermediate helicate with moderately interacting substituents; (C) short helicate with strongly interacting substituents.

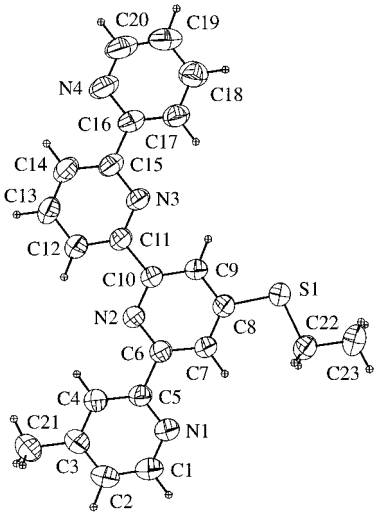



**Figure 10.** Proton NMR shifts of H-3′ and H-5′ in dicopper(I)−qtpy helicates: (A) 4′,4″-bis(methylthio)-qtpy[19]; (B) $[Cu_2(\mathbf{1a})_2][PF_6]_2$; (C) $[Cu_2(\mathbf{1b})_2][PF_6]_2$; (D) $[Cu_2(\mathbf{1c})_2][PF_6]_2$; (E) $[Cu_2(\mathbf{1d})_2][PF_6]_2$. Shifts of the **HH** and **HT** isomers from the same positions are connected by a line.

in the $^1H$ NMR spectroscopic shifts of the anisotropically affected protons. The signals of H-3′ and H-5′ are convenient to monitor this phenomenon, since these absorptions are *invariant* in the qtpy ligands **1a**−**d** and the pairing of these shifts to their respective isomers was possible for the helicate $[Cu_2(\mathbf{1b})_2][PF_6]_2$ (see Figure 10). It should be noted, however, that the presence of separate and distinct absorptions for H-3′ and H-5′ of each isomer of these helicates implies that different anisotropic environments for these protons are present and, thus, that stacking effects are present in these compounds. Models show that in the **HH**-configured helicates the 4-alkyl-4′-(alkylthio)bipyridine ring systems are parallel to the unsubstituted bipyridine ring systems, whereas in the **HT**-configured helicates, comparable interactions occur between identically substituted 2,2′-bipyridine ring systems.

The above points are emphasized by comparison of the helicates from **1f** and **1g**. Here, **HH**−**HT** selectivity similar to that of **1b** (in spite of the highly electronegative ethylsulfonyl and cyano substituents) bespeaks of a steric mechanism, and not one involving stacking effects. Furthermore, the overlap of the proton chemical shifts for H-3′ and H-5′ in the **HH**/**HT** isomers of $[Cu_2(\mathbf{1f})_2][PF_6]_2$ provides evidence of the absence of intrahelical stacking effects.

**Table 3.** Electrochemical Properties of the Dicopper(I) Helicates in Acetonitrile[a]

| | R | R′ | $E_{ox}$ | $E_{red}$ |
|---|---|---|---|---|
| **1a** | H | SMe | 0.435 | 0.116 |
| **1b** | 4-Me | SEt | 0.472 | 0.069 |
| **1c** | 4-Et | SEt | 0.460 | 0.060 |
| **1d** | 4-*t*-Bu | SEt | 0.434 | 0.074 |
| **1e** | 6-Me | SEt | 0.59 | 0.271 |
| **1f** | 4-Me | $SO_2Et$ | 0.637 | 0.202 |
| **1g** | 4-Me | CN | 0.67 | 0.11 |
| **1h** | 4-Me | H | 0.44 | 0.114 |
| **1i** | 4-*t*-Bu | H | 0.48 | 0.073 |

[a] 0.1 M *n*-$Bu_4PF_6$ as supporting electrolyte; all potentials measured relative to ferrocene.

The electrochemical activity of the qtpy helicates from **1a**−**i** has also been investigated in acetonitrile solution (ferrocene/ferrocenium couple as internal standard; see Table 3). Single irreversible oxidation and reduction steps for all of these compounds are observed. However, the precise effect of the various substituents on the separation of the forward and reverse processes is irrevocably linked with both the helical pitch and the electronic character of the substituent. In the absence of detailed data regarding the pitch in each case, we will not discuss these effects further.

## Summary

Asymmetrically alkyl- and alkylthio-substituted qtpy derivatives can be prepared using standard oligopyridine synthetic methodology. Through appropriate substitution of qtpy, it is possible to optimize geometrical parameters of the dicopper(I) helicates, e.g., helical pitch and separation of otherwise spatially remote positions such as to maximize pseudointramolecular interactions between the component helicands. For asymmetrically substituted qtpy derivatives, this can lead to the preferred formation of the **HH** over the **HT** isomer. These processes are correlated through X-ray crystallographic, NMR spectroscopic, and modeling studies. We are further investigating the manifestation of this phenomenon through use of steric and charge-transfer effects with the eventual goal of developing doubly functionalized directional helicates capable of undergoing further self-assembly processes.

## Experimental Section

Infrared spectra were recorded on Mattson Genesis Fourier-transform spectrophotometers with samples in compressed KBr disks. Proton NMR spectra were recorded on a Varian Gemini (300 MHz) or Bruker AC (200 MHz) spectrometer. Carbon NMR spectra were recorded on the former spectrometer (75 MHz). Fast atom bombardment (FAB), chemical ionization (CI), and electron impact (EI) mass spectra were recorded on VG 70−250, Kratos MS-902, and Finnigan 8430 spectrometers; for FAB spectra the sample was loaded using acetonitrile as solvent and 3-nitrobenzyl alcohol as supporting matrix, and the mass value for the most intense signal of an isotopomeric cluster is given. Time of flight (MALDI) spectra were recorded using a PerSeptive Biosystems Voyager-RP biospectrometry workstation. Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 20 system using glassy carbon working and platinum auxiliary electrodes with an Ag/AgCl electrode as reference. The experiments were conducted using purified acetonitrile as solvent and 0.1 M [*n*-$Bu_4N$][$BF_4$] as supporting electrolyte; ferrocene was added at the end of each experiment as an internal reference. Column chromatography was performed with silica gel (70−230 mesh, Fluka) or aluminium oxide, activity III (Fluka).

Diethyl ether and tetrahydrofuran were freshly distilled from sodium−benzophenone ketal, *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide were distilled from calcium hydride under reduced prssure and stored over 4 Å molecular sieves, and dichloromethane was distilled from $P_4O_{10}$. Small amounts of ammonium acetate were dried for 12 h over $P_4O_{10}$ at 200 mbar prior to use. 2-Bromo-4-methylpyridine,[28] 2-bromo-4-ethylpyridine,[29] 2-bromo-6-methylpyridine,[30] 4-*tert*-butyl-2-cyanopyridine,[18] 2-(3′,3′-bis(methylthio)-1′-oxoprop-2′-en-1′-yl)pyridine,[31] and 2-acetyl-6-bromopyridine[32] were obtained according to the literature. All other chemicals were commercially available and were used as received.

**2-Acetyl-4-methylpyridine (5).** A solution of 16.2 g (94 mmol) of 2-bromo-4-methylpyridine in 250 mL of dry $Et_2O$ and under dry nitrogen gas was treated over 20 min at −78 °C with a solution of 57 mL (1.7 M in hexanes, 97 mmol) of *n*-butyllithium. The mixture was stirred for 10 min, and 9.2 mL (99 mmol) of *N*,*N*-dimethylacetamide in 10 mL of $Et_2O$ was added. After stirring for 30 min, warming slowly over 3 h to 25 °C, and stirring for an additional 4 h, water (30 mL) was added. The phases were separated, and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuum. Fractional distillation (84−92 °C, 10 mbar) and recrystallization (pentane, −20 °C) gave 4.69 g (37% yield) of **5** as colorless needles. Mp: ∼25 °C (lit.[29] mp 33−34 °C). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 8.54 (d, $J$ = 9.1 Hz, 1H), 7.86 (s, 1H), 7.29 (dd, $J$ = 0.7; 4.9 Hz, 1H), 2.72 (s, 3H), 2.42 (s, 3H). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ 200.6 (C), 149.51 (C), 148.74 (CH), 127.88 (CH), 124.56 (C), 122.41 (CH), 25.83 ($CH_3$), 21.00 ($CH_3$). IR (film): $\nu$ 833 cm$^{-1}$ (s), 864 (s), 964 (m), 997 (m), 1193 (s), 1288 (s), 1352 (s), 1413 (s), 1603 (s), 1698 (s), 2927 (m), 3009 (m), 3053 (s). EI-MS (70 eV): *m*/*z* (relative intensity) 135 ($M^+$, 79), 107 (27), 93 (100), 92 (68), 66 (26), 65 (31).

**2-(3′,3′-Bis(ethylthio)-1′-oxoprop-2′-en-1′-yl)-4-methylpyridine (9).** To a slurry of 5.2 g (46 mmol) of potassium *tert*-butoxide in 40 mL of dry THF at 0 °C under nitrogen gas was added a solution of 3.0 g (22 mmol) of **5** in 11 mL of THF over 2 min, and then 1.4 mL (23 mmol) of $CS_2$ and 3.6 mL (45 mmol) of iodoethane were added. The cooling bath was removed, and the resulting mixture was stirred overnight at ambient temperature. Crushed ice was then added, and the THF removed by distillation. The remaining solution was left standing at room temperature for ca. 3 h, and the resulting precipitate was collected by filtration and washed with cold ethanol and $Et_2O$. After drying in vacuum over $P_2O_5$, 4.68 g (81%) of **9** as amber needles was obtained. Mp: 108−109 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.49 (d, $J$ = 4.9 Hz, 1H), 8.00 (s, 1H), 7.68 (s, 1H), 7.20 dd, ($J$ = 1.0, 4.8 Hz, 1H), 3.08−3.20 (m, 4H, $-CH_2-$), 2.42 (s, 3H), 1.37−1.47 (m, 6H, $-CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 185.16 (C), 166.28 (C), 158.8 (C), 155.52 (C), 148.86 (CH), 127.27 (CH), 123.99 (CH), 110.27 (CH), 29.0 ($CH_2$), 26.2 ($CH_2$), 21.7 ($CH_3$), 14.4 ($CH_3$), 13.0 ($CH_3$). IR (KBr): $\nu$ 2988 cm$^{-1}$ (w), 2925 (w), 2866 (w), 1594 (m), 1493 (s), 1449 (m), 1268 (w), 1250 (w), 978 (w), 817 (w), 795 (w), 776 (m). CI-MS ($NH_3$): *m*/*z* (relative intensity) 268 (M + 1$^+$, 100), 207 (9), 206 (40), 167 (6), 148 (7).

**2-(3′-(*N*,*N*-Dimethylamino)-1′-oxoprop-2′-en-1′-yl)-4-methylpyridine (12).** A mixture of 2.0 g (15 mmol) of **5** and 4.0 mL (30 mmol) of *N*,*N*-dimethylformamide dimethyl acetal was heated at reflux for 20 h under nitrogen gas. Volatile material was removed *in vacuo*, the remaining crystalline residue was dissolved in EtOAc and decolorized (charcoal), and after repeated crystallization from EtOAc−hexane, 1.73 g (61%) of **12** as yellow leaves was obtained. Mp: 131.8−132.2 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.45 (d, $J$ = 4.9 Hz, 1H), 7.95 (s, 1H), 7.87 (d, $J$ = 12.6 Hz, 1H), 7.14 (d, $J$ = 4.4 Hz, 1H), 6.41 (d, $J$ = 12.7 Hz, 1H), 3.14 (s, 3H), 2.96 (s, 3H), 2.38 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 186.91 (C), 155.89 (C), 151.46 (CH), 147.98 (CH), 147.71 (C), 126.13 (CH), 122.62 (CH), 91.22 (CH), 44.94 ($CH_3$), 37.28 ($CH_3$), 20.91 ($CH_3$). IR (KBr): $\nu$ 3049 cm$^{-1}$ (w), 3010 (w), 2914 (w), 2879 (w), 2812 (w), 1639 (s), 1562 (s), 1547 (s), 1439 (m), 1423 (m), 1354 (s), 1286 (m), 1263 (m), 1122 (m), 1099 (m), 1072 (m), 864 (m), 795 (m), 775 (m). EI-MS (70 eV): *m*/*z* (relative intensity)

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190 ($M^+$, 21), 175 (13), 147 (75), 119 (5), 107 (11), 98 (100), 92 (20), 70 (9), 65 (11).

**2-Acetyl-4-ethylpyridine (6).** A solution of 5.0 g (27 mmol) of 2-bromo-4-ethylpyridine in ca. 70 mL of dry $Et_2O$ and under dry nitrogen gas was treated over 30 min at −78 °C with a solution of 20 mL (1.6 M in hexanes, 32 mmol) of *n*-butyllithium. The mixture was stirred for 15 min, and then 3.5 mL (38 mmol) of *N*,*N*-dimethylacetamide was added. The mixture was warmed to ambient temperature overnight and quenched with a saturated aqueous $NH_4Cl$ solution (30 mL). The phases were separated, and the aqueous solution was extracted with EtOAc (2 × 20 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Column chromatography (15:85 EtOAc−$CH_2Cl_2$/silica gel) gave 3.06 g (76%) of **6** as a light brown oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.56 (d, $J$ = 4.9 Hz, 1H), 7.90 (d, $J$ = 0.8 Hz, 1H), 7.30 (dd, $J$ = 0.9, 3.9 Hz, 1H), 2.68−2.74 (m, 5H), 1.28 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 200.32 (C), 153.99 (C), 153.54 (C), 148.84 (CH), 126.65 (CH), 121.12 (CH), 28.16 ($CH_2$), 25.80 ($CH_3$), 14.14 ($CH_3$). IR (film): $\nu$ 3051 cm$^{-1}$ (w), 2970 (m), 2933 (m), 2875 (m), 1699 (s), 1601 (s), 1462 (m), 1417 (m), 1379 (w), 1354 (m), 1284 (m), 847 (m). EI-MS (70 eV): *m*/*z* (relative intensity) 149 ($M^+$, 68), 121 (16), 107 (100), 106 (95), 92 (7), 79 (26), 77 (26).

**2-Acetyl-4-*tert*-butylpyridine (8).** To a solution of 4.97 g (31 mmol) of 4-*tert*-butyl-2-cyanopyridine in 50 mL of dry $Et_2O$ was slowly added a solution of methylmagnesium iodide (from 1.94 g (80 mmol) of magnesium shavings and 5.0 mL (80 mmol) of iodomethane) in 25 mL of $Et_2O$ at −15 °C. The resulting mixture was stirred for 2.5 h at 25 °C and then quenched with a saturated aqueous $NH_4Cl$ solution. The phases were separated, and the aqueous solution was extracted with EtOAc (3 × 25 mL). The combined organic extracts were washed with water (3 × 10 mL) and once with brine (10 mL) and dried ($MgSO_4$). Removal of the solvent under reduced pressure and purification by column chromatography ($CH_2Cl_2$/silica gel) gave 2.46 g (45% yield) of **8** as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.59 (d, $J$ = 5.2 Hz, 1H), 8.07 (dd, $J$ = 0.6, 2.0 Hz, 1H), 7.47 (dd, $J$ = 5.2, 2.0 Hz, 1H), 2.73 (s, 3H), 1.35 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 200.55 (C), 161.19 (C), 153.57 (C), 148.92 (CH), 124.12 (CH), 118.68 (CH), 34.98 (C), 30.45 ($CH_3$). IR (film): $\nu$ 2966 cm$^{-1}$ (s), 2871 (m), 1699 (s), 1597 (s), 1546 (m), 1479 (m), 1410 (m), 1367 (m), 1352 (m), 1292 (m), 1238 (s), 1132 (m), 862 (m). EI-MS (70 eV): *m*/*z* (relative intensity) 177 ($M^+$, 79), 162 (29), 149 (25), 135 (100), 134 (56), 120 (26), 104 (7), 91 (14), 77 (12). Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 75.38; H, 8.60; N, 7.88.

**Ethyl 2-Pyridyl Sulfoxide (3).** To a solution of 11 g (99 mmol) of 2-mercaptopyridine in 100 mL of aqueous 1 M NaOH was added 8.1 mL (100 mmol) of iodoethane. The mixture was stirred vigorously overnight and then extracted with $Et_2O$ (3 × 50 mL). The combined ethereal extracts were washed with 2 N NaOH (2 × 30 mL) and once with brine and dried ($MgSO_4$). Evaporation of solvent *in vacuo* gave 12.2 g (89%) of 2-(2-mercaptoethyl)pyridine as a pale orange oil. This was dissolved in 185 mL of MeOH, and 26 g (44 mmol, 85% purity) of magnesium monoperoxyphthalate was added in several portions while the temperature was maintained at 0 °C. The mixture was stirred overnight and carefully concentrated by rotary evaporation (water bath temperature below 50 °C) to give a viscous slurry. $H_2O$ (200 mL) was added, and the resulting mixture was extracted with $CHCl_3$ (3 × 30 mL). The combined extracts were washed with brine (2 × 30 mL) and dried ($MgSO_4$). Solvent removal under reduced pressure gave 11.5 g (75% from 2-mercaptopyridine) of **3** as a pale yellow oil, which was >95% pure according to $^1$H NMR spectroscopy and which was used without further purification. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.62 (dd, $J$ = 1.6, 4.7 Hz, 1H), 8.00 (dt, $J$ = 1.1, 7.5 Hz, 1H), 7.93 (dt, $J$ = 1.7, 7.6 Hz, 1H), 7.37 (ddd, $J$ = 1.5, 4.7, 7.3 Hz, 1H), 3.15−3.22 (m, 1H), 2.90−2.97 (m, 1H), 1.20 (t, $J$ = 7.4 Hz, 3H). IR (film): $\nu$ 3050 cm$^{-1}$ (s), 2979 (s), 2934 (s), 1577 (s), 1562 (m), 1452 (m), 1424 (s), 1054 (s), 1025 (m), 991 (m), 782 (m), 769 (m), 540 (m). EI-MS (70 eV): *m*/*z* (relative intensity) 155 ($M^+$, 7), 138 (4), 127 (29), 107 (24), 96 (8), 79 (100), 78 (94), 67 (25).

**6-Bromo-2-(2′-methyl-1′,3′-dioxolan-2′-yl)pyridine (2).** A solution of 1.0 g (5 mmol) of 6-acetyl-2-bromopyridine, 0.34 mL (6 mmol) of 1,2-ethanediol, and 0.1 g (0.5 mmol) of 4-toluenesulfonic acid in 15 mL of benzene was heated for 24 h under reflux in a Dean-Stark apparatus. The mixture was cooled to room temperature, 5 mL of 0.5 M aqueous NaOH solution was added, and the phases were separated. The aqueous phase was washed with benzene (5 mL), and the combined organic extracts were washed with 0.5 M aqueous NaOH (2 × 3 mL) and water (2 × 3 mL) and dried ($MgSO_4$-$K_2CO_3$). After removal of the solvent in vacuo and bulb-to-bulb distillation (90−100 °C, 0.15 mbar) 0.98 g (81%) of **2** as a pale yellow oil was obtained. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.49−7.58 (m, 2H), 7.41 (dd, $J$ = 2.0, 6.8 Hz, 1H), 4.04−4.15 (m, 2H), 3.84−3.95 (m, 2H), 1.72 (s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 162.48 (C), 141.99 (C), 138.75 (CH), 127.48 (CH), 118.20 (CH), 107.98 (C), 65.06 ($CH_2$, C-9), 25.07 (CH, 8-C). IR (film): $\nu$ 2988 (m), 2887 (m), 1578 (s), 1556 (s), 1493 (s), 1400 (s), 1370 (m), 1284 (m), 1232 (w), 1201 (s), 1159 (m), 1131 (m), 1103 (m), 1077 (w), 1038 (s), 986 (m), 950 (m), 875 (m), 800 (s), 744 (m), 708 (m), 648 (w), 629 (w). CI-MS (70 eV, $NH_3$): *m*/*z* (relative intensity) 244 ($M + 1^+$, 100), 200 (4.5), 166 (20), 87 (33).

**6-Acetyl-2,2′-bipyridine (4).** A slurry of 3.10 g (12.7 mmol) of **2** in 100 mL of dry $Et_2O$ was cooled in a methanol/liquid nitrogen bath under dry nitrogen gas and treated with 9.5 mL (1.6 M in hexanes, 15 mmol) of *n*-butyllithium at such a rate that the temperature within the reaction vessel was maintained below −70 °C. After being stirred for 45 min at −40 °C, the mixture was cooled to −70 °C and treated with 3.5 g (23 mmol) of **3**. The intensely red colored mixture was stirred overnight at ambient temperature and quenched with a saturated aqueous $NH_4Cl$ solution (40 mL). The organic phase was separated, the aqueous phase was extracted with EtOAc (2 × 30 mL), and the combined organic extracts were evaporated under vacuum. The remaining red oil was stirred for 3 h at 60 °C in 2 M HCl (60 mL) and cooled to room temperature, EtOAc (20 mL) was added, and the mixture was carefully neutralized by addition of solid $NaHCO_3$. The resulting mixture was extracted with EtOAc (4 × 30 mL), and the organic extracts were combined, washed repeatedly with water and then once with brine, and dried ($MgSO_4$). After removal of the solvent under reduced pressure, the residual solid was purified by column chromatography (15:85 EtOAc−$CH_2Cl_2$/silica gel) and recrystallization (hexanes) to give 1.66 g (67%) of **4** as pale yellow blocks. Reaction of 8.1 g of **2** under similar conditions gave **4** in 59% yield. Mp: 74.7−75.3 °C (lit.[16] mp 74−75.5 °C). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.67 (dm, $J$ = 4.8 Hz, 1H), 8.59 (dd, $J$ = 1.2, 7.8 Hz, 1H), 8.49 (d, $J$ = 8 Hz, 1H), 8.02 (dd, $J$ = 1.2, 7.7 Hz, 1H), 7.90, (t, $J$ = 7.8 Hz, 1H), 7.82 (dt, $J$ = 1.7, 7.7 Hz, 1H), 7.31 (ddd, $J$ = 1.2, 4.7, 7.5 Hz, 1H), 2.81 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 200.04 (C), 155.35 (C), 155.27 (C), 152.87 (C), 149.20 (CH), 137.72 (CH), 136.90 (CH), 124.21 (CH), 124.09 (CH), 121.36 (CH), 121.03 (CH), 25.68 ($CH_3$). IR (KBr): $\nu$ 3001 cm$^{-1}$ (w), 1694 (s), 1580 (s), 1431 (s), 1356 (s), 1314 (m), 1227 (w), 992 (w), 779 (s), 744 (w), 592 (w). EI-MS (70 eV): *m*/*z* (relative intensity) 198 ($M^+$, 85), 170 (26), 156 (100), 155 (97), 130 (17), 78 (35).

**6-(3″-(*N*,*N*-Dimethylamino)-1″-oxoprop-2″-en-1″-yl)-2,2′-bipyridine (13).** A mixture of 1.0 g (5.1 mmol) of **4** and 2.0 mL (15 mmol) of *N*,*N*-dimethylformamide dimethyl acetal was heated to reflux for 28 h under nitrogen gas. The mixture was cooled to 25 °C, whereupon a crystalline mass separated. This material was collected by filtration, washed with cold methanol, and dried over $P_2O_5$ *in vacuo* to give 0.94 g of **13** as orange needles. Volatile material was removed from the method liquor by rotary distillation, and the residual material was recrystallized from EtOAc−hexanes to give an additional 0.16 g (85% total yield) of **13**. Mp: 127.5−128 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.69 (d, $J$ = 4.8 Hz, 1H), 8.50−8.52 (m, 2H), 8.18 (d, $J$ = 7.7 Hz, 1H), 7.91−7.99 (m, 2H), 7.84 (dt, $J$ = 1.7, 7.7 Hz, 1H), 7.32 (ddd, $J$ = 1.3, 2.7, 7.5 Hz, 1H), 6.66 (d, $J$ = 12.4 Hz, 1H), 3.19 (s, 3H), 3.06 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 186.77 (C), 155.96 (C), 155.39 (C), 154.53 (CH), 149.02 (CH), 137.49 (CH), 136.70 (CH), 123.63 (CH), 122.60 (CH), 121.88 (CH), 120.94 (CH), 91.18 (CH), 45.00 ($CH_3$), 37.23 ($CH_3$). IR (KBr): $\nu$ 2914 cm$^{-1}$ (w), 2802 (w), 1645 (s), 1595 (s), 1581 (s), 1549 (s), 1475 (m), 1425 (s), 1414 (s), 1360 (s), 1250 (m), 1084 (m), 1059 (m), 989 (m), 914 (m), 777 (s), 748 (m), 719 (w). EI-MS (70 eV): *m*/*z* (relative intensity) 253 ($M^+$, 13), 238 (5), 236 (6), 210 (38), 170 (51), 155 (24), 98 (100), 78 (10), 70 (6). Anal. Calcd for $C_{15}H_{15}N_3O$: C, 71.13; H, 5.97; N, 16.59. Found: C, 70.54; H, 5.94; N, 16.26.

**6-(3″,3″-Bis(ethylthio)-1″-oxoprop-2″-en-1″-yl)-2,2′-bipyridine (11).** To a suspension of 1.9 g (17 mmol) of potassium *tert*-butoxide in 20

mL of dry THF was slowly added a solution of 1.5 g (7.6 mmol) of **4** in 10 mL of THF. The mixture was stirred for 2 h at ambient temperature, whereupon 0.54 mL (9.1 mmol) of $CS_2$ and 1.4 mL (18 mmol) of iodoethane were added. The mixture was stirred overnight and poured into 100 mL of $H_2O$, and EtOAc (30 mL) was added. The organic phase was separated, and the aqueous phase was extracted (3 × 20 mL) with EtOAc. The combined organic solutions were washed with water (3 × 15 mL) and once with brine (15 mL), dried ($MgSO_4$), and concentrated in vacuum to give 2.38 g of a dark red solid. Recrystallisation (EtOH, 2×) afforded 1.61 g of **11** as yellow needles. Column chromatography (20:80 $NHEt_2$−hexanes/silica gel) of the mother liquor gave an additional 0.11 g of the product (69% total yield) and 0.10 g of **4**. Mp: 109−110 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.70 (dd, $J$ = 0.8, 4.8 Hz, 1H), 8.44 (dd, $J$ = 1.1, 7.9 Hz, 1H), 8.46 (d, $J$ = 8.0 Hz, 1H), 8.20 (dd, $J$ = 1.1, 7.7 Hz, 1H), 7.96 (t, $J$ = 7.8 Hz, 1H), 7.90 (s, 1H), 7.84 (dt, $J$ = 1.8, 7.8 Hz, 1H), 7.34 (ddd, $J$ = 1.1, 4.8, 7.5 Hz, 1H), 3.20 (q, $J$ = 7.4 Hz, 2H), 3.14 (q, $J$ = 7.4 Hz, 2H), 1.53 (t, $J$ = 7.4 Hz, 3H), 1.41 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 184.14 (C), 165.53 (C), 155.74 (C), 154.68 (C), 154.28 (C), 149.19 (CH), 137.91 (CH), 136.75 (CH), 123.83 (CH), 123.14 (CH), 122.53 (CH), 120.66 (CH), 109.33 (CH), 28.30 ($CH_2$), 25.61 ($CH_2$), 13.84 ($CH_3$), 12.82 ($CH_3$). IR (KBr): $\nu$ 3070 cm$^{-1}$ (w), 2968 (w), 2927 (w), 2868 (w), 1620 (m), 1578 (m), 1485 (s), 1448 (s), 1427 (s), 1215 (m), 1092 (m), 1065 (m), 980 (w), 781 (s). CI-MS (70 eV, $NH_3$): *m*/*z* (relative intensity) 331 ($M + 1^+$, 100).

**2-(3′,3′-Bis(ethylthio)-1′-oxoprop-2′-en-1′-yl)-6-methylpyridine (10).** A solution of 44 mL (1.6 M in hexanes, 70 mmol) of *n*-butyllithium was added over 20 min at −70 °C to a slurry of 10 g (58 mmol) of 2-bromo-6-methylpyridine in 150 mL of dry $Et_2O$. The mixture was stirred for 30 min at this temperature, and 7.2 mL (77 mmol) of *N*,*N*-dimethylacetamide was slowly added. The mixture was stirred 1 h at −40 °C and then at ambient temperature overnight and finally heated under reflux for 6 h. A saturated aqueous $NH_4Cl$ solution (30 mL) and then EtOAc (30 mL) were added, and the phases were separated. The aqueous layer was extracted with EtOAc (3 × 10 mL), and the combined organic extracts were washed with water (3 × 20 mL) and once with brine (20 mL) and dried ($MgSO_4$). Column chromatography (20:80 $NHEt_2$−hexanes/silica gel) gave 5.43 g of a colorless oil, which analyzed (GC−MS) as a 1:1.5 mixture of 2-acetyl-6-methylpyridine (**7**) and 2-bromo-6-methylpyridine. To a slurry of 3.0 g (27 mmol) of potassium *tert*-butoxide in 30 mL of dry THF under nitrogen gas was added a solution of 5.0 g of the above mixture in 10 mL of THF. After stirring for ca. 90 min, 0.80 mL (13 mmol) of $CS_2$ was added. The mixture was cooled to 0 °C, 2.1 mL (26 mmol) of iodoethane was added, and stirring was continued for ca. 48 h at ambient temperature. Then, $CH_2Cl_2$ (20 mL) and water (30 mL) were added to the mixture, the phases were separated, and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic solutions were washed with water (3 × 10 mL) and once with brine (10 mL) and dried ($Na_2SO_4$). After solvent evaporation under reduced pressure, a crystalline mass separated from the crude product. Recrystallization from EtOH gave 1.51 g of **10** as yellow leaves. Chromatography of the mother liquor ($CH_2Cl_2$/silica gel) and subsequent recrystallization gave another 0.11 g (11% total yield from 2-bromo-6-methylpyridine). Mp: 107.5−108.5 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.96 (d, $J$ = 7.7 Hz, 1H), 7.74 (s, 1H), 7.68 (t, $J$ = 7.7 Hz, 1H), 7.23 (d, $J$ = 6.4 Hz, 1H), 3.13 (q, $J$ = 7.4 Hz, 2H), 3.11 (q, $J$ = 7.4 Hz, 2H), 1.45 (t, $J$ = 7.4 Hz, 3H), 1.38 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 184.47 (C), 165.02 (C), 157.10 (C), 154.39 (C), 136.83 (CH), 125.32 (CH), 119.43 (CH), 109.65 (CH), 28.19 ($CH_2$), 25.47 ($CH_2$), 24.40 ($CH_3$), 13.76 ($CH_3$), 12.42 ($CH_3$). IR (KBr): $\nu$ 3113 cm$^{-1}$ (w), 3062 (w), 2972 (m), 2931 (s), 1620 (m), 1585 (m), 1491 (s), 1448 (s), 1254 (m), 1217 (m), 1072 (s), 991 (m), 789 (s), 773 (m). EI-MS (70 eV): *m*/*z* (relative intensity) 238 ($M - SC_2H_5^+$, 4), 206 (100), 178 (19), 175 (5), 120 (26), 92 (53), 85 (11). Anal. Calcd for $C_{13}H_{17}NOS_2$: C, 58.39; H, 6.41; N, 5.24. Found: C, 58.55; H, 6.44; N, 5.47.

**Preparation of Quaterpyridine Ligands. 4-Methyl-4′′-(ethylthio)-2,2′:6′,2′′:6′′,2′′′-quaterpyridine (1b).** To a suspension of 0.56 g (5.0 mmol) of potassium *tert*-butoxide in 3 mL of dry THF under nitrogen gas and cooled in an ice−water bath was added a solution of 0.45 g (2.3 mmol) of **4** in 5 mL of THF. The cooling bath was removed, and 0.61 g (2.3 mmol) of **9** was added. The mixture was stirred for 36 h at ambient temperature, after which 1.8 g (23 mmol) of $NH_4OAc$ and 12 mL of glacial acetic acid were added. The THF was slowly removed by distillation over a period of 3.5 h, and the remaining material was treated with crushed ice. The resulting mixture was treated with PhMe, and the acetic acid was neutralized by addition of a saturated aqueous $NaHCO_3$ solution. Extraction with warm PhMe (5 × 40 mL), washing of the combined organic solutions with water (5 × 10 mL) and once with brine (10 mL), drying ($MgSO_4$), and solvent evaporation under reduced pressure gave a crude product. This material was dissolved in $CH_2Cl_2$, passed through aluminum oxide, decolorized with bone charcoal (hexane), and recrystallized (EtOH) to give 0.27 g (31%) of **1b** as pale yellow needles. Mp: 164−165 °C. $^1$H NMR (70% $(CD_3)_2$SO−30% $CDCl_3$, 300 MHz): $\delta$ 8.41−8.70 (m, 7H), 8.29 (d, $J$ = 1 Hz, H-3′/H-5′), 8.05 (t, $J$ = 7.1 Hz, H-4′′), 7.95 (dt, $J$ = 1.7, 6.0 Hz, H-4′′′), 7.41−7.43 (m, H-5′′′), 7.22 (d, $J$ = 4.3 Hz, H-5), 3.23 (q, $J$ = 7.4 Hz, H-8′), 2.49 (s, H-7), 1.47 (t, $J$ = 7.4 Hz, H-9′). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 156.21 (C), 155.73 (C), 155.28 (C), 155.24 (C), 155.16 (C), 154.94 (C), 151.13 (C), 149.11 (CH), 148.86 (CH), 147.95 (C), 137.75 (CH), 136.86 (CH), 124.84 (CH), 123.74 (CH), 122.16 (CH), 121.33 (CH), 121.14 (CH), 121.08 (CH), 118.05 (CH), 117.65 (CH), 25.16 ($CH_2$, 8′-C), 21.33 ($CH_3$, 7-C), 13.80 ($CH_3$, 9′-C). $^{13}$C NMR (70% $(CD_3)_2$SO−30% $CDCl_3$, 75 MHz): $\delta$ 155.04, 154.60, 154.51, 154.17, 150.53, 148.70, 148.43, 147.43, 137.58, 136.66, 124.64, 123.69, 123.62, 121.33, 120.82, 120.62, 120.34, 116.85, 116.77, 24.26 ($CH_3$, 9′-C), 20.71 ($CH_3$, 7-C), 13.34 ($CH_2$, 8′-C). IR (KBr): $\nu$ 3051 cm$^{-1}$ (w), 2972 (w), 2925 (m), 2850 (w), 1603 (w), 1562 (s), 1537 (m), 1475 (m), 1458 (m), 1425 (m), 1375 (m), 829 (m), 785 (s), 754 (m), 660 (m). EI-MS (70 eV): *m*/*z* (relative intensity) 384 ($M^+$, 76), 369 (17), 356 (100), 351 (32), 324 (31), 312 (15), 205 (12), 192 (11), 178 (13), 155 (9). Anal. Calcd for $C_{23}H_{20}N_4S$: C, 71.85; H, 5.24; N, 14.57. Found: C, 72.18; H, 5.29; N, 14.32.

**4′-(Methylthio)-2,2′:6′,2′′:6′′,2′′′-quaterpyridine (1a).** To a stirred suspension of 0.57 g (5.0 mmol) of potassium *tert*-butoxide in 10 mL of dry THF under nitrogen gas at 0 °C was added a solution of 0.50 g (2.5 mmol) of **4** in 5 mL of THF. The cooling bath was removed, and after 30 min at ambient temperature, 0.57 g (2.5 mmol) of 2-(3′,3′-bis(methylthio)-1′-oxoprop-2′-en-1′-yl)pyridine was added. After stirring overnight, 1.0 g (13 mmol) of $NH_4OAc$ and 10 mL of acetic acid were added, and the THF was slowly removed by distillation over 5 h. The AcOH was then distilled off at water aspirator pressure to leave a dark-colored gum. This material was dissolved in a mixture of saturated aqueous $NaHCO_3$ solution and $CH_2Cl_2$, the phases were separated, and the aqueous layer was extracted with $CH_2Cl_2$ (5 × 20 mL). The combined organic extracts were washed with saturated $NaHCO_3$ solution (3 × 10 mL) and once with brine (10 mL) and dried ($Na_2SO_4$). Column chromatography (40:60 $NHEt_2$−hexanes/silica gel and then PhMe/aluminium oxide) and recrystallization (PhMe) afforded 0.35 g (39%) of **1a** as pale yellow microcrystals. Mp: 145.5−146 °C. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 156.2 (C), 155.3 (C), 155.09 (C), 155.03 (C), 154.83 (C), 152.18 (C), 149.14 (CH), 149.03 (CH), 137.81 (CH), 136.90 (CH), 136.47 (CH), 123.90 (CH), 123.79 (CH), 121.48 (CH), 121.44 (CH), 121.36 (CH), 121.16 (CH), 117.33 (CH), 116.64 (CH), 14.08 ($CH_3$, 8′-C). IR (KBr): $\nu$ 3057 cm$^{-1}$ (w), 2999 (w), 2920 (w), 1577 (m), 1558 (s), 1543 (s), 1471 (m), 1460 (m), 1425 (m), 1392 (s), 1269 (m), 1092 (m), 1072 (m), 825 (m), 783 (s), 598 (m). EI-MS (70 eV): *m*/*z* (relative intensity) 356 ($M^+$, 100), 355 (37), 311 (9), 310 (29), 309 (5), 232 (1), 205 (11), 182 (3), 178 (7), 170 (1), 162 (1), 156 (3). Anal. Calcd for $C_{21}H_{16}N_4S$: C, 70.76; H, 4.52; N, 1572. Found: C, 70.51; H, 4.59; N, 15.79.

**4-Ethyl-4′-(ethylthio)-2,2′:6′,2′′:6′′,2′′′-quaterpyridine (1c).** The preparation of this compound was analogous to that of compound **1a** from 0.41 g (2.8 mmol) of **6**, 0.70 g (2.1 mmol) of **11**, 0.68 g (6.1 mmol) of potassium *tert*-butoxide, 2.2 g (29 mmol) of $NH_4OAc$, and 14 mL of glacial acetic acid. Column chromatography (20:80 $NHEt_2$−hexanes/silica gel and then 60:40 $CHCl_3$−PhMe/aluminium oxide) gave 0.021 g of **11** and 0.50 g (60%) of **1c** after recrystallization of the latter (EtOAc−pentane). Mp: 141.5−141.8 °C. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 156.06 (C), 155.70 (C), 155.19 (C), 155.14 (C), 155.01 (C), 154.77 (C), 153.78 (C), 151.01 (C), 149.00 (CH), 148.89 (CH), 137.64 (CH), 136.75 (CH), 123.64 (CH), 123.46 (CH), 121.21 (CH), 121.03 (CH), 120.97 (CH), 120.88 (CH), 117.87 (CH), 117.52 (CH), 28.43 ($CH_2$, 7/8′-C), 25.04 ($CH_2$, 7/8′-C), 14.41 ($CH_3$, 8/9′-C), 13.70 ($CH_3$, 8/9′-C). IR (KBr): $\nu$ 3076 cm$^{-1}$ (w), 2968 (m), 2929 (m), 2871 (w), 1562 (s), 1537 (s), 1471 (m), 1456 (m), 1428 (s), 1385 (s), 1319

(w), 1261 (m), 849 (m), 787 (s), 771 (s). EI-MS (70 eV): *m*/*z* (relative intensity) 398 ($M^+$, 100), 397 (37), 383 (10), 371 (20), 370 (79), 369 (14), 365 (20), 338 (17), 205 (9), 199 (10), 185 (8), 155 (8). Anal. Calcd for $C_{24}H_{22}N_4S$: C, 72.33; H, 5.56; N, 14.06. Found: C, 72.01; H, 5.53; N, 14.02.

**4-*tert*-Butyl-4′-(ethylthio)-2,2′:6′,2″:6″,2‴-quaterpyridine (1d).** The preparation of this compound was analogous to that of compound **1a** from 0.71 g (2.2 mmol) of **11**, 0.50 g (2.8 mmol) of **8**, 0.63 g (5.6 mmol) of potassium *tert*-butoxide, 2.2 g (29 mmol) of $NH_4OAc$, and 14 mL of glacial acetic acid. Column chromatography (20:80 $NHEt_2$−hexanes/silica gel) afforded 0.13 g of **11** and 0.31 g (33%) of **1d** after recrystallization (hexanes) of the latter compound. Mp: 137.5−138.5 °C. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 160.87 (C), 156.17 (C), 155.80 (C), 155.50 (C), 155.24 (C), 155.09 (C), 154.81 (C), 151.08 (C), 149.09 (CH), 148.96 (CH), 137.81 (CH), 136.87 (CH), 123.74 (CH), 121.14 (CH), 121.06 (CH), 118.28 (CH), 117.96 (CH), 117.68 (CH), 34.96 (C, 7-C), 30.62 ($CH_3$, 8-C), 25.13 ($CH_2$, 8′-C), 13.78 ($CH_3$, 9′-C). IR (KBr): $\nu$ 3062 $cm^{-1}$ (w), 2964 (m), 2927 (m), 2864 (m), 1564 (s), 1542 (s), 1473 (m), 1460 (m), 1423 (m), 1377 (s), 1327 (w), 989 (w), 870 (w), 843 (w), 825 (m), 783 (m), 744 (m), 660 (m). EI-MS (70 eV): *m*/*z* (relative intensity) 426 ($M^+$, 100), 425 (37), 412 (14), 411 (49), 399 (16), 398 (59), 393 (14), 384 (11), 370 (22), 250 (5), 213 (10), 205 (12), 198 (9), 192 (6), 184 (4). Anal. Calcd for $C_{26}H_{26}N_4$: C, 73.21; H, 6.14; N, 13.13. Found: C, 73.37; H, 6.19; N, 13.07.

**6-Methyl-4′-(ethylthio)-2,2′:6′,2″:6″,2‴-quaterpyridine (1e).** The preparation of this compound was analogous to that of compound **1a** from 0.54 g (2.0 mmol) of **10**, 0.40 g (2.0 mmol) of **4**, 0.45 g (4.0 mmol) of potassium *tert*-butoxide, 1.3 g (17 mmol) of $NH_4OAc$, and 8 mL of glacial acetic acid. After column chromatography (20:80 $NHEt_2$−hexanes/silica gel and then 60:40 $CHCl_3$−PhMe/aluminium oxide) and recrystallization ($CHCl_3$−pentane), 0.37 g (46%) of **1e** was obtained as colorless plates. Mp: 127.5−128 °C. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 157.67 (C), 156.12 (C), 155.25 (C), 155.21 (C), 155.11 (C), 155.08 (C), 154.81 (C), 150.87 (C), 149.14 (CH), 137.76 (CH), 136.99 (CH), 136.89 (CH), 123.77 (CH), 123.42 (CH), 121.37 (CH), 121.16 (CH), 121.08 (CH), 118.44 (CH), 117.75 (CH), 25.22 ($CH_2$, 8′-C), 24.73 ($CH_3$, 7-C), 13.86 ($CH_3$, 9′-C). IR (KBr): $\nu$ 3049 $cm^{-1}$ (w), 2974 (m), 2927 (m), 2871 (w), 1562 (s), 1543 (s), 1458 (s), 1429 (m), 1396 (s), 1263 (m), 1126 (m), 1082 (m), 984 (m), 874 (m), 810 (m), 779 (s). EI-MS (70 eV): *m*/*z* (relative intensity) 385 ($M^+$, 80), 383 (10), 369 (16), 356 (100), 355 (10), 351 (31), 324 (31), 323 (8), 312 (15), 205 (12), 192 (10), 178 (11), 155 (8), 142 (6). Anal. Calcd for $C_{23}H_{20}N_4S$: C, 71.85; H, 5.24; N, 14.57. Found: C, 71.41; H, 5.22; N, 14.54.

**4-Methyl-4′-(ethylsulfonyl)-2,2′:6′,2″:6″,2‴-quaterpyridine (1f).** A mixture of 0.41 g (1.1 mmol) of **1b** and 0.43 g (2.1 mmol, 85% pure) of 3-chloroperbenzoic acid in 5 mL of $CH_2Cl_2$ was stirred overnight at ambient temperature. At the end of that time, the solvent was removed under reduced pressure, and the residual material was dissolved in $CHCl_3$. The organic solution was washed with a saturated $NaHCO_3$ solution (5 × 8 mL) and once with brine and dried ($Na_2SO_4$). Recrystallization (4:1 EtOH−EtOAc) afforded 0.34 g (74%) of **1f** as fine yellow needles. Mp: 203−204.5 °C. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 157.72 (C), 157.44 (C), 155.86 (C), 155.68 (C), 154.27 (C), 153.78 (C), 149.30 (CH), 149.17 (CH), 148.97 (C), 148.30 (C), 138.07 (CH), 137.12 (CH), 125.68 (CH), 124.06 (CH), 122.23 (CH), 122.01 (CH), 121.40 (CH), 118.73 (CH), 118.30 (CH), 50.09 ($CH_2$, 8′-C), 29.69 ($CH_3$, 7/9′-C), 7.19 ($CH_3$, 7/9′-C). IR (KBr): $\nu$ 3095 $cm^{-1}$ (w), 2931 (w), 2850 (w), 1604 (w), 1560 (s), 1375 (m), 1317 (s), 1269 (m), 1143 (s), 827 (m), 785 (m), 723 (m), 660 (w), 534 (m). EI-MS (70 eV): *m*/*z* (relative intensity) 416 ($M^+$, 30), 352 (11), 351 (15), 324 (100), 323 (10), 205 (14), 182 (3), 162 (8), 155 (9), 142 (10). Anal. Calcd for $C_{23}H_{20}N_4O_2S$: C, 66.33; H, 4.84; N, 13.45. Found: C, 66.22; H, 5.06; N, 13.20.

**4-Methyl-4′-cyano-2,2′:6′,2″:6″,2‴-quaterpyridine (1g).** A mixture of 0.22 g (0.54 mmol) of **1f** and 0.38 g (6 mmol) of potassium cyanide in 8 mL of dry DMF was heated under reflux for 96 h under nitrogen gas. The mixture was poured into a brine solution (30 mL) and extracted with $CHCl_3$ (3 × 5 mL). The combined organic extracts were washed with water (3 × 5 mL) and once with brine and dried ($Na_2SO_4$). After solvent removal under reduced pressure, recrystallization (EtOH−EtOAc) gave 0.16 g (83%) of **1g** as beige plates. Mp: 189.7−190.4 °C. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 200.45 (C, 7′-C), 156.74 (C), 156.50 (C), 155.62 (C), 155.56 (C), 153.88 (C), 153.29 (C), 149.14 (CH), 148.30 (C), 138.00 (CH), 136.95 (CH), 125.66 (CH), 123.99 (CH), 122.48 (CH), 122.28 (CH), 121.95 (CH), 121.92 (CH), 121.14 (CH), 121.05 (CH), 117.11 (C), 21.32 ($CH_3$, 7-C). IR (KBr): $\nu$ 3059 $cm^{-1}$ (w), 2924 (m), 2853 (m), 2235 (w), 1595 (m), 1577 (m), 1552 (s), 1459 (m), 1391 (m), 1375 (m), 1268 (m), 1082 (m), 988 (m), 888 (m), 828 (m), 790 (s), 749 (m), 661 (m). EI-MS (70 eV): *m*/*z* (relative intensity) 349 ($M^+$, 100), 348 (18), 324 (3), 323 (2), 321 (4), 271 (3), 257 (2), 244 (1), 230 (2), 192 (2), 174 (6), 155 (4). Anal. Calcd for $C_{22}H_{15}N_5$: C, 75.63; H, 4.33; N, 20.04. Found: C, 75.33; H, 4.52; N, 19.79.

**4-Methyl-2,2′:6′,2″:6″,2‴-quaterpyridine (1h).** The preparation of this compound was analogous to that of compound **1a** from 0.67 g (3.4 mmol) of **4**, 0.65 g (3.4 mmol) of **12**, 0.83 g (7.4 mmol) of potassium *tert*-butoxide, 1.4 g (18 mmol) of $NH_4OAc$, and 4.5 mL of glacial acetic acid. After column chromatography (10:90 $NHEt_2$−hexanes/silica gel and then 60:40 $CHCl_3$−hexanes/aluminum oxide) and recrystallization (EtOH), 0.102 g (9.3%) of **1h** as colorless plates was obtained. Mp: 175.5−176.5 °C. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 156.26 (C), 156.02 (C), 155.50 (C), 155.46 (C), 155.38 (C), 155.33 (C), 149.11 (CH), 148.95 (CH), 147.99 (C), 137.79 (CH), 137.75 (CH), 136.85 (CH), 124.75 (CH), 123.74 (CH), 121.94 (CH), 121.19 (CH), 121.16 (CH), 121.06 (CH), 120.96 (CH), 21.35 ($CH_3$, 7-C). IR (KBr): $\nu$ 3051 $cm^{-1}$ (m), 2999 (w), 2943 (w), 1606 (m), 1577 (s), 1566 (s), 1473 (m), 1446 (m), 1423 (s), 1400 (m), 1269 (m), 989 (m), 814 (m), 781 (s), 754 (m), 658 (m), 633 (m). EI-MS (70 eV): *m*/*z* (relative intensity) 324 ($M^+$, 100), 323 (28), 309 (3), 298 (3), 297 (3), 282 (2), 261 (2), 259 (1), 246 (6), 244 (2), 232 (5), 230 (2), 219 (3), 205 (3), 169 (5), 162 (5), 155 (6). Anal. Calcd for $C_{21}H_{16}N_4$: C, 77.76; H, 4.97; N, 17.27. Found: C, 77.00; H, 4.98; N, 17.08.

**4-*tert*-Butyl-2,2′:6′,2″:6″,2‴-quaterpyridine (1i).** The preparation of this compound was analogous to that of compound **1a** from 0.56 g (3.2 mmol) of **8**, 1.05 g (4.2 mmol) of **13**, 0.95 g (8.5 mmol) of potassium *tert*-butoxide, 1.6 g (21 mmol) of $NH_4OAc$, and 5.2 mL of glacial acetic acid. After column chromatography (PhMe and then 10:90 $NHEt_2$−hexanes, both on aluminum oxide) and recrystallization (hexanes), 0.26 g (22%) of **1i** as pale yellow microcrystals was obtained. Mp: 122−123 °C. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 160.83 (C), 156.20 (C), 156.06 (C), 155.72 (C), 155.36 (C), 155.27 (C), 155.21 (C), 149.05 (CH), 137.80 (CH), 137.71 (CH), 136.81 (CH), 123.70 (CH), 121.15 (CH), 120.93 (CH), 120.87 (CH), 120.83 (CH), 118.01 (CH), 34.94 (C, 7-C), 30.60 ($CH_3$, 8-C). IR (KBr): $\nu$ 3059 $cm^{-1}$ (w), 2966 (m), 2868 (w), 1592 (w), 1566 (s), 1473 (m), 1425 (m), 1400 (m), 1271 (m), 1109 (w), 814 (m), 779 (s), 752 (w), 658 (w). EI-MS (70 eV): *m*/*z* (relative intensity) 366 ($M^+$, 88), 365 (58), 351 (100), 349 (5), 345 (5), 344 (4), 335 (6), 324 (12), 310 (39), 309 (14), 289 (4), 282 (3), 232 (5), 205 (3), 183 (6), 176 (10), 175 (14). Anal. Calcd for $C_{24}H_{22}N_4$: C, 78.66; H, 6.05; N, 15.29. Found: C, 78.53; H, 6.03; N, 15.13.

**General Preparation of the Dicopper(I) Helicates of Ligands 1a−i.** Mixtures of **1a**−**i** and tetrakis(acetonitrile)copper(I) hexafluorophosphate were heated in degassed methanol under reflux under an atmosphere of $N_2$ or Ar (**1d**, **1h** and **1i**) for 30−60 min. After this, the qtpy ligands had dissolved and deep red solutions had been obtained. Methanolic ammonium hexafluorophosphate was added to the hot solutions, and after 1−2 h at room temperature, the supernatant solvent was removed with a pipet. The precipitated complexes were washed twice with cold methanol and dried under vacuum. The crude complexes were recrystallized after filtration of a solution through a small amount of Celite.

**$[Cu_2(1a)_2][PF_6]_2$.** Combination of 30 mg (0.084 mmol) of **1a**, 31 mg (0.084 mmol) of $[(CH_3CN)_4Cu][PF_6]$ in 3 mL of MeOH, and 250 mg of $[NH_4][PF_6]$ resulted in 21 mg (44% yield) of the product after recrystallization (2×) from MeCN−$Et_2O$. IR (KBr): $\nu$ 3093 $cm^{-1}$ (w), 1601 (s), 1462 (m), 1437 (w), 1419 (w), 1402 (w), 1327 (w), 1252 (w), 1167 (w), 1117 (w), 1230 (m), 840 (s), 783 (m), 557 (s). FAB-MS (NBA): *m*/*z* (relative intensity) 984 (4.1, $Cu_2$(**1a**)$_2$), 440 (4.9, Cu(**1a**)). Anal. Calcd for $C_{42}H_{32}Cu_2F_{12}N_8P_2S_2$: C, 44.65; H, 2.85; N, 9.92. Found: C, 44.0; H, 3.6; N, 9.7.

**$[Cu_2(1b)_2][PF_6]_2$.** Combination of 50 mg (0.13 mmol) of **1b**, 47 mg (0.13 mmol) of $[(CH_3CN)_4Cu][PF_6]$ in 7 mL of MeOH, and 250 mg $[NH_4][PF_6]$ resulted in 63 mg (82% yield) of the product. The sample for the combustion analysis was twice recrystallized from

MeCN−$Et_2O$. $^1H$ NMR (300 MHz, $(CD_3)_2SO$): $\delta$ 7.61−8.26 (m, 10H), 7.36−7.40 (m, $H^B$-5‴), 7.29−7.33 (m, $H^A$-5‴), 7.22 (d $J$ = 4.4 Hz, $H^A$-5), 7.14 (d, $J$ = 4.9 Hz, $H^B$-5), 3.24 (q, $J$ = 7.1 Hz, H-8′), 2.49 (s, $H^A$-7), 2.44 (s, $H^B$-7), 1.41 (t, $J$ = 7.1 Hz, H-9′). $^{13}C$ NMR (75 MHz, $(CD_3)_2SO$): $\delta$ 153.12, 153.00, 152.86, 152.61, 150.86, 150.80, 150.54, 150.43, 150.26, 150.11, 150.01, 149.85, 149.24, 148.96, 148.14, 147.81, 138.40, 137.55, 137.37, 127.02, 126.88, 126.38, 126.10, 125.58, 125.49, 122.84, 122.14, 122.08, 121.825, 120.94, 120.54, 117.34, 24.16 ($CH_2$, 8′-C), 20.94 ($CH_3$, 7-$C^A$), 20.66 ($CH_3$, 7-$C^B$), 13.52 ($CH_3$, 9′-$C^B$), 13.40 ($CH_3$, 9′-$C^A$). IR (KBr): $\nu$ 2958 $cm^{-1}$ (w), 2914 (w), 1588 (s), 1535 (w), 1452 (m), 1413 (w), 1379 (w), 1240 (w), 1118 (w), 840 (s), 774 (m), 557 (s). FAB-MS (NBA): *m*/*z* (relative intensity) 1041 (5.7, $Cu_2$(**1b**)$_2$), 449 (52.7, Cu(**1b**)). Anal. Calcd for $C_{46}H_{40}Cu_2F_{12}N_8P_2S_2$: C, 46.58; H, 3.40; N, 9.45. Found: C, 45.77; H, 3.50; N, 9.19.

**[$Cu_2$(1c)$_2$][$PF_6$]$_2$.** Combination of 10 mg (0.025 mmol) of **1c**, 10 mg (0.027 mmol) of [$(CH_3CN)_4Cu$][$PF_6$] in 4 mL of MeOH, and 100 mg of [$NH_4$][$PF_6$] resulted in 12 mg (79% yield) of the product after recrystallization (2×) from MeCN−$Et_2O$. IR (KBr): $\nu$ 2970 $cm^{-1}$ (w), 2873 (w), 1587 (m), 1456 (m), 1404 (w), 1383 (w), 1119 (w), 839 (s), 777 (m), 557 (m). TOF-MS (5000 V; 2,3-dihydroxybenzoic acid matrix): *m*/*z* 1070 ($Cu_2$(**1c**)$_2$). Anal. Calcd for $C_{48}H_{44}Cu_2F_{12}N_8P_2S_2$: C, 47.49; H, 3.65; N, 9.23. Found: C, 46.95; H, 3.47; N, 9.35.

**[$Cu_2$(1d)$_2$][$PF_6$]$_2$.** Combination of 41 mg (0.096 mmol) of **1d**, 44 mg (0.12 mmol) of [$(CH_3CN)_4Cu$][$PF_6$] in 7 mL of MeOH, and 200 mg of [$NH_4$][$PF_6$] resulted in 10 mg (16% yield) of the product after recrystallization (2×) from MeOH−$Et_2O$. IR (KBr): $\nu$ 2966 $cm^{-1}$ (w), 2873 (w), 1589 (m), 1543 (w), 1483 (w), 1456 (m), 1383 (m), 1275 (w), 1117 (m), 841 (m), 77 (m), 557 (s). FAB-MS (NBA): *m*/*z* (relative intensity) 1127 (5.4, $Cu_2$(**1d**)$_2$($PF_6$)), 980 (2.0, $Cu_2$(**1d**)$_2$), 489 (100, Cu(**1d**)). Anal. Calcd for $C_{52}H_{52}Cu_2F_{12}N_8P_2S_2$: C, 49.17; H, 4.13; N, 8.82. Found: C, 48.66; H, 4.28; N, 8.77.

**[$Cu_2$(1e)$_2$][$PF_6$]$_2$.** Combination of 30 mg (0.078 mmol) of **1e**, 35 mg (0.094 mmol) of [$(CH_3CN)_4Cu$][$PF_6$] in 5 mL of MeOH, and 300 mg of [$NH_4$][$PF_6$] resulted in 38 mg (82% yield) of the product. The sample for the combustion analysis was twice recrystallized from MeCN−$Et_2O$. $^1H$ NMR (300 MHz, $(CD_3)_2SO$): $\delta$ 7.58−8.33 (m, 10H), 7.34−7.46 (m, H-5, H-5‴), 2.49−3.24 (m, 8′-H), 1.91 (s, $H^A$-7), 1.80 (s, $H^B$-7), 1.37−1.41 (m, H-9′). $^{13}C$ NMR (75 MHz, $(CD_3)_2SO$): $\delta$ 156.31 (C), 156.03 (C), 153.44 (C), 153.41 (C), 152.94 (C), 152.85 (C), 150.72 (C), 150.54 (C), 150.27 (C), 150.05 (C), 149.89 (C), 149.65 (C), 148.55 (CH), 148.47 (CH), 138.54 (CH), 138.38 (CH), 137.75 (CH), 137.64 (CH), 137.56 (CH), 126.42 (CH), 126.14 (CH), 126.01 (CH), 125.94 (CH), 125.20 (CH), 124.70 (CH), 122.24 (CH), 122.05 (CH), 121.98 (CH), 121.78 (CH), 120.45 (CH), 120.04 (CH), 119.74 (CH), 117.55 (CH), 24.82 ($CH_3$, 7-$C^A$), 24.56 ($CH_3$, 7-$C^B$), 24.13 ($CH_2$, 8′-C), 13.44 ($CH_3$, 9′-C). IR (KBr): $\nu$ 1597 $cm^{-1}$ (m), 1576 (m), 1541 (w), 1460 (m), 1396 (w), 1136 (w), 1011 (w), 841 (s), 781 (m), 557 (m). FAB-MS (NBA): *m*/*z* (relative intensity) 1041 (5.7, $Cu_2$(**1e**)$_2$($PF_6$)), 896 (3.5, $Cu_2$(**1e**)$_2$), 447 (77, Cu(**1e**)). Anal. Calcd for $C_{46}H_{40}Cu_2F_{12}N_8P_2S_2$: C, 46.58; H, 3.40; N, 9.45. Found: C, 46.28; H, 3.47; N, 9.63.

**[$Cu_2$(1f)$_2$][$PF_6$]$_2$.** Combination of 30 mg (0.072 mmol) of **1f**, 32 mg (0.086 mmol) of [$(CH_3CN)_4Cu$][$PF_6$] in 4.5 mL of MeOH, and 300 mg of [$NH_4$][$PF_6$] resulted in 35 mg (78% yield) of the product. The sample for the combustion analysis was twice recrystallized from MeCN−$Et_2O$. IR (KBr): $\nu$ 3078 $cm^{-1}$ (w), 2925 (w), 1612 (m), 1597 (m), 1458 (m), 1406 (m), 1319 (m), 1236 (w), 1149 (m), 841 (s), 719 (w), 559 (m). FAB-MS (NBA): *m*/*z* (relative intensity) 1102 (6.6, $Cu_2$(**1f**)$_2$($PF_6$)), 959 (5.9, $Cu_2$(**1f**)$_2$), 479 (100, Cu(**1f**)). Anal. Calcd for $C_{46}H_{40}Cu_2F_{12}N_8O_4P_2S_2$: C, 44.20; H, 3.23; N, 8.96. Found: C, 43.18; H, 3.35; N, 8.70.

**[$Cu_2$(1g)$_2$][$PF_6$]$_2$.** Combination of 30 mg (0.086 mmol) of **1g**, 32 mg (0.09 mmol) of [$(CH_3CN)_4Cu$][$PF_6$] in 3.5 mL of MeOH, and 300 mg of [$NH_4$][$PF_6$] resulted in 26 mg (54% yield) of the product after recrystallization (2×) from MeCN−$Et_2O$. Partial decomposition of this material was evident from the $^1H$ NMR spectrum. IR (KBr): $\nu$ 3093 $cm^{-1}$ (w), 2929 (w), 2241 (w), 1612 (m), 1545 (w), 1458 (m), 1415 (m), 1234 (w), 843 (s), 779 (m), 557 (m). FAB-MS (NBA): *m*/*z* (relative intensity) 971 (2.4, $Cu_2$((**1g**)$_2$($PF_6$)), 826 (1.7, $Cu_2$((**1g**)$_2$), 412 (100, Cu((**1g**)). Anal. Calcd for $C_{44}H_{30}Cu_2F_{12}N_{10}P_2$: C, 47.36; H, 2.71; N, 12.55. Found: C, 44.84; H, 3.13; N, 11.44.

**[$Cu_2$(1h)$_2$][$PF_6$]$_2$.** Combination of 30 mg (0.093 mmol) of **1h**, 36 mg (0.097 mmol) of [$(CH_3CN)_4Cu$][$PF_6$] in 6 mL of MeOH, and 120 mg of [$NH_4$][$PF_6$] resulted in 20 mg (41%) of the product after recrystallization (2×) from MeCN−diisopropyl ether. IR (KBr): $\nu$ 1616 $cm^{-1}$ (m), 1597 (m), 1508 (w), 1458 (m), 1431 (w), 1404 (w), 1294 (w), 1018 (w), 841 (s), 777 (m), 696 (w), 557 (m). FAB-MS (NBA): *m*/*z* (relative intensity) 776 (4.3, $Cu_2$(**1h**)$_2$), 387 (100, Cu(**1h**)). Anal. Calcd for $C_{42}H_{32}Cu_2F_{12}N_8P_2$: C, 47.33; H, 3.03; N, 10.51. Found: C, 46.70; H, 2.99; N, 10.46.

**[$Cu_2$(1i)$_2$][$PF_6$]$_2$.** Combination of 30 mg (0.082 mmol) of **1i**, 31 mg (0.08 mmol) of [$(CH_3CN)_4Cu$][$PF_6$] in 3 mL of MeOH, and 200 mg of [$NH_4$][$PF_6$] resulted in 39 mg (83%) of the product after recrystallization (2×) from MeCN−$Et_2O$. IR (KBr): $\nu$ 2970 $cm^{-1}$ (m), 1597 (m), 1568 (m), 1460 (m), 1429 (w), 1379 (w), 1252 (w), 839 (s), 777 (m), 754 (w), 557 (m). FAB-MS (NBA): *m*/*z* (relative intensity) 1005 (5.4, $Cu_2$(**1i**)$_2$($PF_6$)), 860 (3.3, $Cu_2$(**1i**)$_2$), 429 (100, Cu(**1i**)). Anal. Calcd for $C_{48}H_{44}Cu_2F_{12}N_8P_2$: C, 50.14; H, 3.86; N, 9.74. Found: C, 49.62; H, 3.99; N, 9.62.

**X-ray Structure Determination of 1b and 1h.** Compounds **1b** and **1h** crystallize as cube-shaped, colorless crytals. Samples were attached with glue on a glass fiber and mounted on the diffractometer. Unit cell parameters were determined by carefully centering 25 independent, strong reflections with 22.60° ≤ $\theta$ ≤ 42.67° (**1b**) and 23.25° ≤ $\theta$ ≤ 45.63° (**1h**). Data collection was carried out at room temperature using an Enraf-Nonius CAD4 diffractometer equipped with a Cu Kα fine-focus sealed tube and with a graphite monochromator. Reflections with 2.56° ≤ $\theta$ ≤ 74.33° (**1b**) and 2.38° ≤ $\theta$ ≤ 77.50° (**1h**) were measured. No significant intensity loss was observed during either data collection.

The usual corrections were applied to both, and absorption correction was carried out using DIFABS.[33] The structure of **1b** was solved by direct methods using the program SHELXS-86,[34] and that of **1h** was likewise solved using the program SIR92.[35] Anisotropic least squares full matrix refinement for both was carried out on all non-hydrogen atoms using the program CRYSTAL;[36] hydrogen atoms are in calculated positions. Parameter refinement for both was implemented with $I > 3\sigma(I)$ and completed using Chebychev weights.[37] Scattering factors were taken from the International Tables, Vol. IV, Table 2.2B. The fractional coordinates have been deposited at the Cambridge Crystallographic Data Center. The data and parameters used are summarized in Table 2.

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**Supporting Information Available:** Tables giving crystal data, atomic hydrogen atom coordinates, isotropic and anisotropic displacement parameters, and bond lengths and angles for 4-methyl-4′-(ethylthio)-qtpy and 4-methyl-qtpy (11 pages). See any current masthead page for ordering and Internet access instructions.

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