Synthesis and Characterization of New Substituted Terdentate 2,6-Bis(2'-quinolinyl)pyridine and 1,3-Bis(2'-quinolinyl)-benzene Ligands for Transition Metals

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Received May 17, 1999

A series of N-N-N terdendate polypyridine type ligands and their N-C-N cyclometalating homologues were synthetized and fully characterized (L_1-L_{12}). Complete assignments of the ^1H spectra of the various compounds, accomplished by using a combination of one- and two-dimensional nmr techniques, and ^{13}C data are also reported.

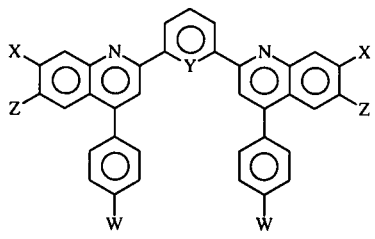
J. Heterocyclic Chem., **37**, 1225 (2000).

Luminescent and redox-active polypyridine-type metal complexes are playing a key role as molecular components (building blocks) in the development of supramolecular species capable of harvesting solar energy and elaborating light information at the molecular level [1]. Most studies concern Ru(II) and Os(II) complexes containing bidentate ligands such as 2,2'-bipyridine (bpy) [2]. Terdentate ligands (*e.g.*; 2,2':6',2"-terpyridine, terpy) [3] have some advantage over bidentate ligands as far as the structural properties of octahedral metal complexes are concerned in that terdentate ligands lead to stereochemically defined achiral species, whereas bidentate ligands can give rise to stereoisomerism at six-coordinated metal centers [4]. As a consequence, terdentate polypyridine-type ligands are particularly interesting as far as the control of the geometry of supramolecular structures is concerned. However, the use of terdentate polypyridine ligands has often been a two-edged sword, in that distortion of the octahedral skeleton decreases the energy of metal-centered excited states leading to complexes having excited states which are usually short-lived and rarely emissive at room temperature [4].

The problem of having complexes rarely emissive at room temperature, has recently been overcome by using electron-withdrawing [5] and ethynyl [6] substituents on the terpyridine skeleton and terdentate ligands that exhibit an extended conjugation [7]. In this regard, the cyclometalation approach has been successfully employed [8]. In all cases, a key to obtain room temperature luminescence from Ru(II) and/or Os(II) terdentate complexes is to increase the energy gap between the luminescent MLCT level and the upper-lying MC excited state [9-11] or to use a different transition metal [12].

In order to overcome the above problems, we have synthesized a series of terdendate polypyridine ligands exhibiting an extended conjugation, bearing π-activating or deactivating groups, and/or a cyclometalation binding site. Such ligands in principle, can act as a terdentate ligands to chelate a metal ion by employing either (i) the three nitrogen atoms (see L_1, L_3, L_5, L_7, L_9, and L_{11}) or (ii) two nitrogens and the C-2 atom of the central benzene ring (see L_2, L_4, L_6, L_8, L_{10}, and L_{12}), giving rise to cyclometalation (Scheme I).

Scheme I

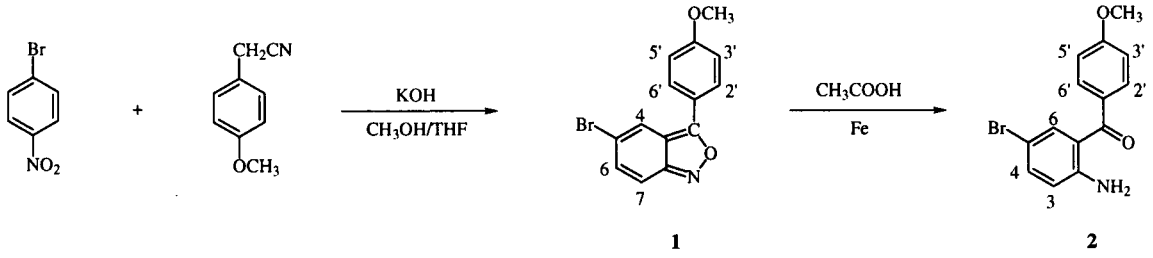


Ligands	Y	Z	X	W	Initials
L_1	N	H	H	H	**bpqpy**
L_2	CH	H	H	H	**bpqb-H**
L_3	N	H	CH_3	H	**bmpqpy**
L_4	CH	H	CH_3	H	**bmpqb-H**
L_5	N	NO_2	H	H	**bnpqpy**
L_6	CH	NO_2	H	H	**bnpqb-H**
L_7	N	$NHCOCH_3$	H	H	**bapqpy**
L_8	CH	$NHCOCH_3$	H	H	**bapqb-H**
L_9	N	Br	H	OCH_3	**bbpqpy**
L_{10}	CH	Br	H	OCH_3	**bbpqb-H**
L_{11}	N	CN	H	OCH_3	**bcpqpy**
L_{12}	CH	CN	H	OCH_3	**bcpqb-H**

Here we report the synthesis and characterization of most of the ligands showed in Scheme I. All the compounds were characterized by elemental analysis, ei or fab mass, and ^1H and ^{13}C nmr spectroscopies. Complete assignments of the ^1H spectra of the various compounds were accomplished by using a combination of one- and two-dimensional nmr techniques.

2-Amino-5-bromo-4'-methoxybenzophenone (**2**) required for the synthesis of ligands L_9 [2,6-bis(6'-bromo-4'-*p*-methoxyphenyl-2'-quinolinyl)pyridine (**bbpqpy**)] and L_{10} [2,6-bis(6'-bromo-4'-*p*-methoxyphenyl-2'-quinolinyl)benzene (**bbpqb-H**)] was obtained in two steps by condensation of *p*-nitrobromobenzene with *p*-methoxyphenylacetonitrile in a basic methanol/tetrahydrofuran (THF) medium to give 3-(4'-methoxypheny)-5-bromo-2,1-benzisoxazole **1** (64%), which upon reductive cleavage (Fe/CH_3COOH) of the benzoisoxazole ring (Scheme II) was converted to the desired aminoketone **2** (66%). The Friedlander reaction [13] of the appropriate *ortho*-aminobenzophenone with 2,6-diacetylpyridine or 1,3-diacetylbenzene, using a mixture of *m*-cresol and

Scheme II



1 2

phosphorous pentoxide as solvent and catalyst at 135°, gave ligands L_1, L_3, L_5, L_9, and the cyclometalating homologues L_2, L_4, L_6, L_{10}, respectively.

The ligands L_7 [2,6-bis(6'-acetylamino-4'-phenyl-2'-quinolinyl)pyridine (**bapqpy**)], and L_8 [2,6-bis(6'-acetylamino-4'-phenyl-2'-quinolinyl)benzene (**bapqb-H**)], were synthesized by reductive acetylation (iron in acetic acid and acetic anhydride) of L_5 [2,6-bis(6'-nitro-4'-phenyl-2'-quinolinyl)pyridine (**bnpqpy**)], and L_6 [2,6-bis(6'-nitro-4'-phenyl-2'-quinolinyl)benzene (**bapqb-H**)], respectively. Treating **bbpqpy** and **bbpqb-H** with cupric cyanide in *N*-methylpyrrolidone at 200° gave ligands L_{11} [2,6-bis(6'-cyano-4'-*p*-methoxyphenyl-2'-quinolinyl)pyridine (**bcpqpy**)] and L_{12} [2,6-bis(6'-cyano-4'-phenyl-2'-quinolinyl)benzene (**bcpqb-H**)] respectively, in good yields.

Table 1 reports the results of a complete ^1H nmr analysis of ligands L_1-L_{12}. Proton chemical shift and J(H,H) values were measured on a 500 MHz ^1H nmr instrument. Assignments were aided by the use of 2D homonuclear chemical shift correlated ^1H nmr (COSY) [14]. As an example, the Figure shows the COSY-45 experiment of L_2 [2,6-bis(4'-phenyl-2'-quinolinyl)benzene (**bpqb-H**)] and includes as the upper trace the related ^1H nmr spectrum, both run in 1,1,2,2-tetrachloroethane-d_2 (TCE). The two signals at 9.02 and 7.96 ppm were easily assigned by the integration ratio to H^2 and $H^{3'}$, respectively. Furthermore, the peak at 9.02 ppm is correlated with the 2H double doublet at 8.30 ppm that in turn is correlated to the 1H triplet at 7.72 ppm. This first-order four spin system is easily assigned to the benzene protons H^2, $H^4(H^6)$, and H^5. Another four-spin system is identified, through the COSY spectrum, as connecting the signals at 8.35, 7.95, 7.79, and 7.60 ppm. The broad doublet (*ortho* coupling) at 8.35 ppm and the double triplet at 7.79 ppm have been assigned to $H^{8'}$ and $H^{7'}$, respectively, by comparison with literature ^1H data for L_1 [15]. $H^{5'}$ and $H^{6'}$ resonances could be assigned at 7.95 and 7.60 ppm, respectively. It is worth noting that *ortho*, *mesa*, and *para* cross-peaks are observable in the COSY-45 spectrum and can be distinguished from the number and/or the intensity of the spots.

Table 2 shows the upfield or downfield shift on the resonance of the various protons when the central benzene ring is replaced by a pyridine moiety. As expected protons H^4, H^5, and H^6 of benzene moiety (owing to the different numbering of the N-N-N terdendate ligands with respect to the N-C-N cyclometalating homologues, these correspond to H^3, H^4, and H^5 in the pyridine ring) experience a downfield shift due to the behavior of pyridine similar to a highly deactivated benzenic derivative. The highest downfield shift experienced by the $H^{3'}$ protons, due to deshielding by the non-bonding electrons of the nitrogen on the opposite ring, is suggestive of an *anti-anti* conformation for the ligands, in agreement with the conformation considered the most probable for terpyridine [3]. The resonance of the remaining quinoline protons, as expected, show a negligible sensitivity to the replacement of the central benzene moiety by the pyridine ring.

Table 1

^{1}H NMR Parameters of Ligands L_1-L_{12} (Chemical Shifts in ppm Downfield from Tetramethylsilane and Coupling Constants in Hz) [a,b,c]

Proton	**bpqpy** L_1	**bpqb-H** L_2	**bmpqpy** L_3	**bmpqb-H** L_4	**bnpqpy** L_5	**bnpqb-H** L_6	**bapqpy** L_7	**bapqb-H** L_8	**bbpqpy** L_9	**bbpqb-H** L_{10}	**bcpqpy** L_{11}	**bcpqb-H** L_{12}
2		9.02 bs		8.98 bs		9.11 bs		8.95 bs		8.95 bs		9.04 bs
3	8.83 d		8.76 d		8.90 d		8.74 d		8.77 d		8.84 d	
	J = 8.0		J = 7.8		J = 8.0		J = 7.5		J = 8.0		J = 8.0	
4	8.12 t	8.30 dd	8.09 t	8.29 d	8.18 t	8.44 d	8.07 d	8.26 d	8.09 t	8.27 dd	8.14 t	8.35 dd
	J = 7.5	J = 7.5; 2.0	J = 7.5	J = 7.5	J = 7.5	J = 8.0	J = 7.5	J = 8.5	J = 7.5	J = 7.5; 1.5	J = 8.0	J = 8.0; 1.5
5	8.83 d	7.72 t	8.76 d	7.71 t	8.90 d	7.77 t	8.74 d	7.68 t	8.77 d	7.70 t	8.84 d	7.74 t
	J = 8.0	J = 8.0	J = 7.8	J = 7.5	J = 8.0	J = 8.0	J = 7.5	J = 8.5	J = 8.0	J = 7.5	J = 8.0	J = 8.0
6		8.30 dd		8.29 d		8.44 d		8.26 d		8.27 dd		8.35 dd
		J = 7.5; 2.0		J = 7.5		J = 8.0		J = 8.5		J = 7.5; 1.5		J = 8.0; 1.5
3'	8.75 s	7.96 s	8.63 s	7.90 s	8.87 s	8.11 s	8.67 s	7.91 s	8.69 s	7.92 s	8.79 s	8.03 s
5'	8.01 d	7.95 d	7.88 d	7.84 d	8.92 d	8.86 d	8.08 bs	8.04 bs	8.15 bs	8.10 bs	8.40 bs	8.36 s
	J = 8.0	J = 7.5	J = 8.5	J = 8.5	J = 2.5	J = 2.5						
6'	7.66 m	7.60 dt	7.36 dd	7.36 d								
		J = 8.5; 1.0	J = 8.6; 1.8	J = 8.5								
7'	7.78 bt	7.79 dt			8.52 dd	8.51 dd	7.93 bd	7.93 m	7.83 bd	7.84 dd	7.89 bd	7.89 dd
	J = 8.0	J = 8.5; 1.0			J = 9.0; 2.5	J = 9.0; 2.5	J = 9.0		J = 9.0	J = 9.0; 2.0	J = 8.5	J = 8.5; 1.5
8'	8.31 d	8.35 bd	8.06 bs	8.14 bs	8.40 d	8.40 d	8.23 d	8.25 d	8.13 d	8.18 d	8.33 d	8.37 d
	J = 8.5	J = 8.5			J = 9.5	J = 8.0	J = 9.0	J = 8.0	J = 9.0	J = 9.0	J = 8.5	J = 8.5
2"/6"	7.56 m	7.58 m	7.55 m	7.58 m	7.63 bs	7.63	7.64 m	7.58 m	7.56 d	7.52 dd	7.55 d	7.52 d
									J = 8.0	J = 8.5; 2.0	J = 8.5	J = 8.5
3"/5"	7.56 m	7.58 m	7.55 m	7.58 m	7.63 m	7.63 m	7.57 m	7.58 m	7.09 d	7.11 dd	7.11 d	7.14 d
									J = 8.0	J = 8.5; 2.0	J = 8.5	J = 8.5
4"	7.56 m	7.58 m	7.55 m	7.58 m	7.63 m	7.63 m	7.57 m	7.58 m				
CH_3			2.59 s	2.61 s								
OCH_3									3.92 s	3.91 s	3.93 s	3.93 s
NH							7.39 s	7.42 s				
$COCH_3$							2.17 s	2.16 s				

[a] The spectra were obtained in deuterated 1,1,2,2-tetrachloroethane (TCE); [b] Numbering pattern shown in Scheme III; [c] Abbreviations used: bs = broad singlet, s = singlet, d = doublet, dd = double doublet, m = multiplet, t = triplet.

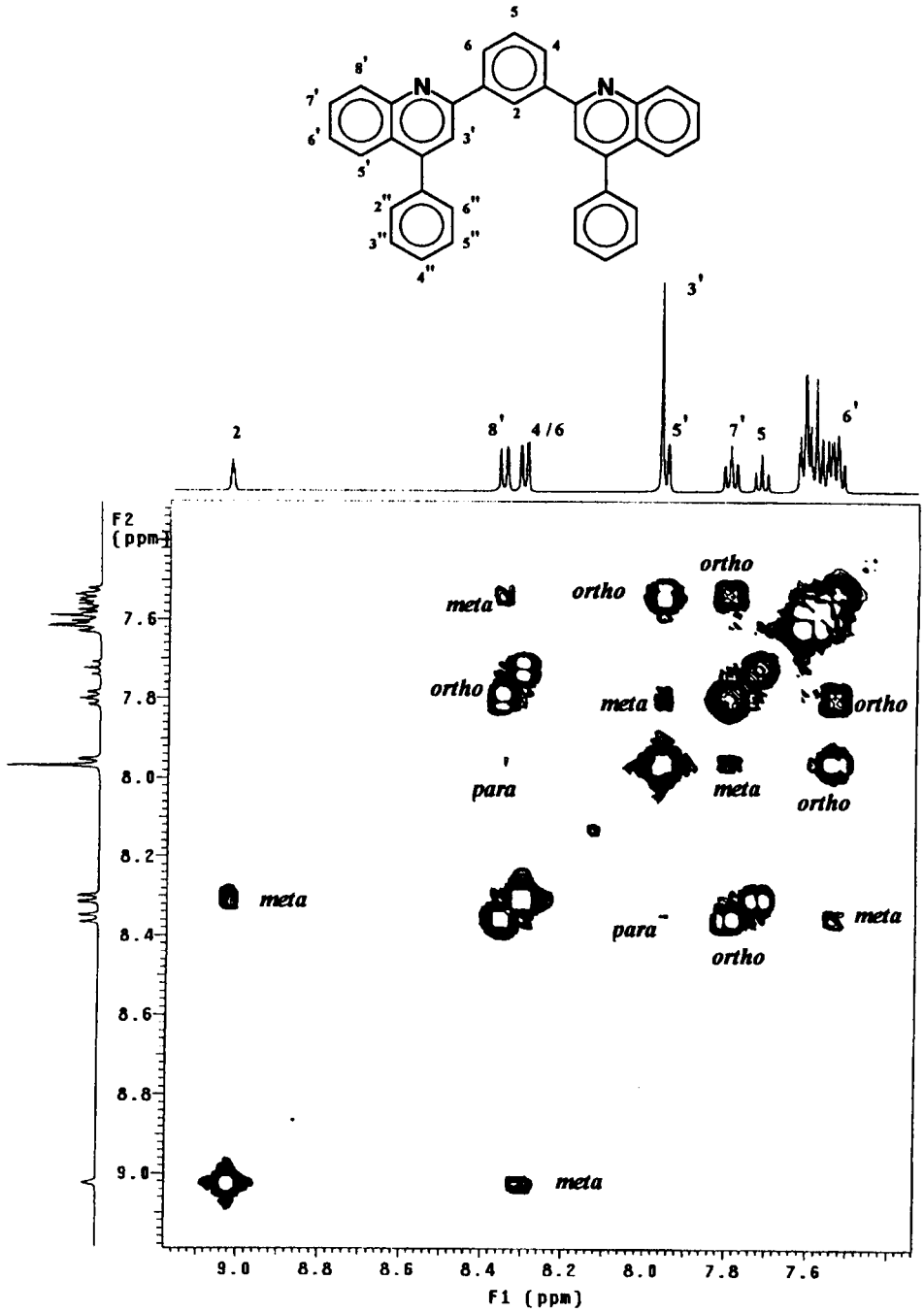


Figure. 500 MHz $^1H/^1H$ COSY-45 spectrum of **bpqb-H** (L_2) in deuterated 1,1,2,2-tetrachloroethane (TCE). The upper and left trace are the 1D proton spectrum of L_2.

According to literature data [15], confirmed by our ^1H nmr analyses, these molecules, if free, show an *anti-anti* conformation (as depicted in Scheme I) that changes to *syn-syn* when they act as ligands by using the nitrogen of the central pyridine ring or the C-2 position of the central benzene ring as a binding site. According to the inductive and/or mesomeric effects of the substituents, their introduction onto the skeleton of the N-N-N terdendate ligand L_1 [2,6- bis(4'-phenyl-2'-quinolinyl)pyridine (**bpqpy**)] and/or its N-C-N cyclometalating homologue **bpqb-H**, influence the chemical reactivity of these molecules as expected.

The structure of ligands L_1-L_{12} was further confirmed by their carbon nmr spectra, which displayed the expected patterns.

Table 2

Upfield ($\Delta\delta < 0$) and Downfield ($\Delta\delta > 0$) Shift of the Various Protons Caused by Substitution of Central Benzene Ring with Pyridine [a]

Proton	L_2/L_1	L_4/L_3	L_6/L_7	L_8/L_7	L_{10}/L_9	L_{12}/L_{11}
3-5/4-6	+0.53	+0.47	+0.46	+0.48	+0.50	+0.49
4/5	+0.40	+0.38	+0.41	+0.39	+0.39	+0.40
3'	+0.79	+0.73	+0.76	+0.76	+0.77	+0.76
5'	+0.06	+0.04	+0.06	+0.04	-0.01	+0.04
6'	+0.06	0.00	–	–	–	–
7'	-0.01	–	+0.01	0.00	-0.01	0.00
8'	-0.04	-0.08	0.00	-0.02	-0.03	-0.04
2"/6"	-0.02	-0.03	0.00	+0.06	+0.04	+0.03
3"/5"	-0.02	-0.03	0.00	-0.01	-0.02	-0.03
4"	-0.02	-0.03	0.00	-0.01	–	–
CH_3		+0.02				
OCH_3					-0.01	0.00
NH				+0.03		
$COCH_3$				-0.01		

[a] Numbering pattern shown in Scheme III.

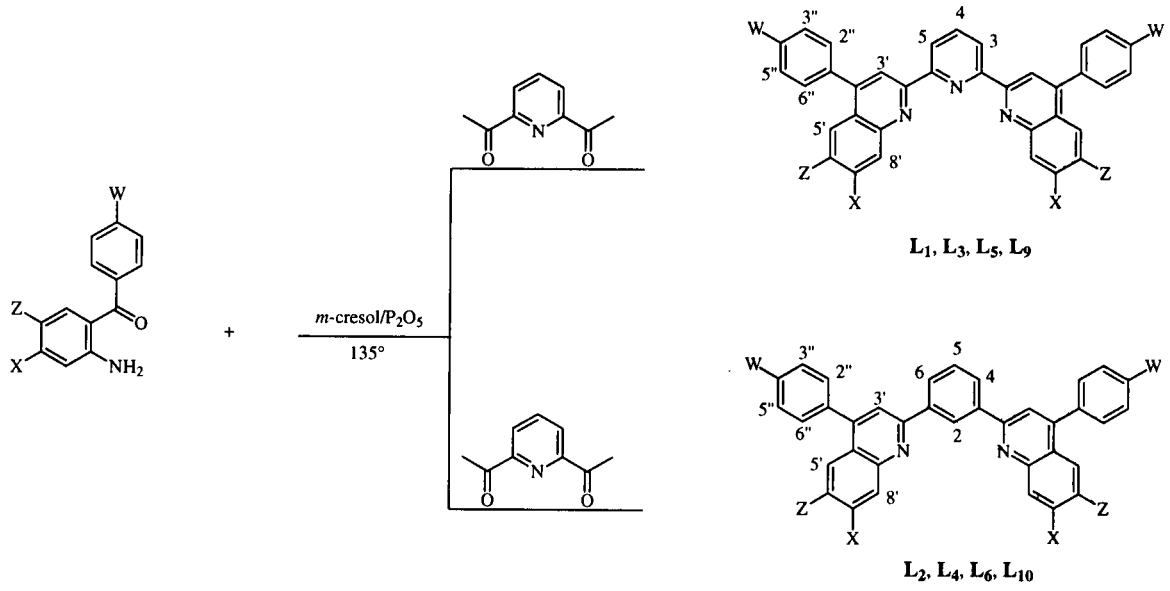
[2,6-bis(6'-methyl-4'-phenyl-2'-quinolinyl)benzene (**bmpqb-H**)], were prepared as described in the literature [9,11]. All reactions were performed under an inert atmosphere of nitrogen except when otherwise stated and the solvents were dried and stored under nitrogen and over 4Å molecular sieves. Melting points are uncorrected. Elemental analyses were determined commercially.

Proton and carbon decoupled (BB 125.7 MHz) nmr spectra were performed in deuterated TCE with a Varian INOVA 500 instrument using tetramethylsilane (TMS) as an internal reference. Positive ion fab mass spectra were obtained on a Kratos MS 50 S double-focusing mass spectrometer equipped with a standard FAB source, using 3-nitrobenzyl alcohol as a matrix.

3-(4'-Methoxyphenyl)-5-bromo-2,1-benzisoxazole (**1**).

To a vigorously stirred solution, constituted by 17.76 g (0.31 mole) of potassium hydroxide in methanol (35 ml) at 0°, was slowly added 2.18 g (0.0148 mole) of *p*-methoxyphenylacetonitrile. After the solution was complete, 36 ml of a solution containing 3.0 g (0.015 mole) of *p*-nitro-bromobenzene in methanol/tetrahydrofuran (2:1, v/v) was added dropwise. The resulting dark mixture was stirred at 0° for 4 hours, at room temperature for 18 hours,

Scheme III



EXPERIMENTAL

The starting materials, 2,6-diacetylpyridine, 1,3-diacetylbenzene, 2-aminobenzophenone, 2-amino-4-methylbenzophenone, 2-amino-5-nitrobenzophenone, *p*-nitrobromobenzene, and (4-methoxyphenyl)acetonitrile were purchased from Aldrich. All other chemicals were reagent grade. The ligands L_1 [2,6-bis-(4'-phenyl-2'-quinolinyl)pyridine (**bpqpy**)], L_3 [2,6-bis-(6'-methyl-4'-phenyl-2'-quinolinyl)pyridine (**bmpqpy**)], and L_4

and then poured into 300 ml of ice-water to afford, after filtration, cold water and methanol washings and methanol recrystallization, **1** as yellow crystals; 2.92 g (64%); mp 127°; ^{1}H nmr (deuteriochloform): δ 8.00 (bs, 1H, H^4 of benzoisoxazole); 7.97 (d, 2H, J = 7.2 Hz, $H^{2'}/H^{6'}$ of phenyl), 7.49 (d, 1H, J = 9.6 Hz, H^6 of benzoisoxazole); 7.35 (d, 1H, J = 9.6 Hz, H^7 of benzoisoxazole); 7.08 (d, 2H, J = 7.2 Hz, $H^{3'}/H^{5'}$ of phenyl); 3.90 (s, 3H, $-OCH_3$); ms, m/z 303 ($M^{+\bullet}$, 89%).

Anal. Calcd. for $C_{14}H_{10}BrNO_2$: C, 55.44; H, 3.30; N, 4.62. Found: C, 55.19; H, 3.13; N, 4.86.

2-Amino-5-bromo-4'-methoxybenzophenone (**2**).

Following the procedure of Simpson and Stephenson [16], a solution, constituted by 0.5 g (0.0016 mole) of **1** in acetic acid (70 ml), was heated on a water-bath, and 1.0 g (0.018 mole) of iron powder was added over 2.5 hours, during which time, 12 ml of water was also added. The mixture was filtered while hot and then 100 ml of water were added. The yellow precipitate was collected by filtration, washed with cold water until the water washings were clear and dried. The product was purified by column chromatography (aluminium oxide; chloroform:ether 1:1) followed by recrystallization from ethanol-water afforded **2** as a yellow powder; 0.42 g (66%); mp 110°; ^{1}H nmr (deuteriochloroform): δ 7.66 (d, 2H, J = 8.5 Hz, $H^{2'}/H^{6'}$ of phenyl); 7.54 (s, 1H, H^6 of benzene); 7.32 (d, 1H, J = 8.10 Hz, H^4 of benzene); 6.95 (d, 2H, J = 8.5 Hz, $H^{3'}/H^{5'}$ of phenyl); 6.61 (d, 1H, J = 8.6 Hz, H^3 of benzene); 5.87 (bs, 2H, of amino), 3.86 (s, 3H, $-OCH_3$); ms, m/z 305 ($M^{+\bullet}$, 88%).

Anal. Calcd. for $C_{14}H_{12}BrNO_2$: C, 55.08; H, 3.93; N, 4.59. Found: C, 55.28; H, 3.59; N, 4.65.

The synthesis of ligand L_5 is given below as a general procedure for the central pyridine ring closure reaction and was the method for the synthesis of ligand 2,6-bis(6'-bromo-4'-*p*-methoxyphenyl-2'-quinolinyl)pyridine (**bbpqpy**, L_9).

2,6-Bis(6'-nitro-4'-phenyl-2'-quinolinyl)pyridine (**bnpqpy**, L_5).

A mixture of *m*-cresol (40 ml) and phosphorus pentoxide (1.62 g) was stirred at 145° for 2.5 hours to afford a homogeneous solution. After cooling, 9.68 g (40.0 mmoles) of 2-amino-5-nitrobenzophenone and 3.26 g (20.0 mmoles) of 2,6-diacetylpyridine were added, with 50 ml of *m*-cresol to rinse the powder funnel. The reaction mixture was heated at 135° overnight. After cooling, the dark solution was poured into 550 ml of ethanol containing 55 ml of triethylamine. The light grey-pink precipitate was collected by filtration, continuosly extracted with a solution of ethanol/triethylamine for 24 hours, and recrystallized from dimethylformamide to give **bnpqpy** as an off-white powder; 10.47 g (91%); mp > 300; ms, m/z 575 ($M^{+\bullet}$, 40%).

Anal. Calcd. for $C_{35}H_{21}N_5O_4$: C, 73.03; H, 3.67; N, 12.17. Found: C, 73.44; H, 3.73; N, 11.72.

The synthesis of ligand L_2 is given below as a general procedure for the central benzene ring closure reaction and was the method for the synthesis of the ligands 2,6-bis(6'-nitro-4'-phenyl-2'-quinolinyl)benzene (**bnpqb-H**, L_6), and 2,6-bis-(6'-bromo-4'-*p*-methoxyphenyl-2'-quinolinyl)benzene (**bbpqb-H**, L_{10}).

1,3-Bis(4'-phenyl-2'-quinolinyl)benzene (**bpqb-H**, L_2).

This ligand was prepared by using the above synthetic procedure. In a typical preparation, 3.23 g (20 mmoles) of 1,3-diacetylbenzene was reacted with 7.88 g (40 mmoles) of 2-aminobenzophenone. Upon recrystallization from ethyl alcohol **bpqb-H** was obtained as a white powder; 6.61g (99%); mp 180°; ms, m/z 488 ($M^{+\bullet}$, 30%).

Anal. Calcd. for $C_{36}H_{24}N_2$: C, 89.22; H, 5.15; N, 5.95. Found: C, 89.22; H, 4.99; N, 5.78.

2,6-Bis(6'-acetylamino-4'-phenyl-2'-quinolinyl)pyridine (**bapqpy**, L_7).

To a stirred and refluxing solution of 2.01 g (3.5 mmoles) of **bnpqpy** in glacial acetic acid (130 ml), 3 g of iron powder was added by portion and the green-black mixture was allowed to reflux for 12 hours. After hot filtration, acetic anhydride (40 ml) addition and reflux for 8 hours, the dark solution was poured into ice/water (500 ml) to obtain, after filtrabon, a yellow powder. The product was added by portion to a 5% w/w stirred water solution of potassium carbonate (130 ml), to get after filtration, several water and methanol washings, and vacuum drying **bapqpy** as an off-white solid; 0.8 g (38%); mp > 250°; ms, m/z 599 ($M^{+\bullet}$, 50%).

Anal. Calcd. for $C_{39}H_{29}N_5O_2 \cdot H_2O$: C, 75.83; H, 5.05; N, 11.33. Found: C, 76.14; H, 4.70; N, 11.41.

2,6-Bis(6'-acetylamino-4'-phenyl-2'-quinolinyl)benzene (**bapqb-H**, L_8).

This ligand was prepared by using the above synthetic procedure. In a typical preparation, 2.01 g (3.5 mmoles) of **bnpqb-H** was reacted in glacial acetic acid with 3 g of iron powder and acetic anhydride. Upon recrystallization from toluene **Bapqb-H** was obtained as a white powder; 1.2 g (57%); mp > 250°; ms, m/z 598 ($M^{+\bullet}$, 60%).

Anal. Calcd. for $C_{40}H_{30}N_4O_2 \cdot 2H_2O$: C, 75.70; H, 5.40; N, 8.83. Found: C, 75.50; H, 5.53; N, 8.77.

2,6-Bis(6'-cyano-4'-*p*-methoxyphenyl-2'-quinolinyl)pyridine (**bcpqpy**, L_{11}).

A mixture of 1.0 g (1.42 mmoles) of **bbpqpy**, 0.50 g (5.68 mmoles) of cupric cyanide, and *N*-methylpyrrolidone (150 ml) was stirred at 200° for 12 hours and then, after cooling at 80°, was poured into 3*N* hydrochloric acid (300 ml) containing 0.92 g (5.68 mmoles) of ferric chloride. The mixture was stirred at room temperature for 2 hours to afford, after filtration, water and methanol washings, and upon recrystallization from toluene, **bcpqpy** as an off-white powder; 0.45 g (53%); mp > 250°; ms, m/z 595 ($M^{+\bullet}$, 40%).

Anal. Calcd. for $C_{39}H_{25}N_5O_2$: C, 78.63; H, 4.23; N, 11.76. Found: C, 78.50; H, 4.53; N, 11.77.

2,6-Bis(6'-cyano-4'-*p*-methoxyphenyl-2'-quinolinyl)benzene (**bcpqb-H**, L_{12}).

This ligand was prepared by using the above synthetic procedure. In a typical preparation, 1.0 g (1.42 mmoles) of **bbpqb-H** was reacted in *N*-methylpyrrolidone (130 ml) with 0.50 g (5.68 mmoles) of cupric cyanide to afford, upon recrystallization from toluene, **bcpqb-H** as an off-white powder; 0.65 g (77%); mp > 250°; ms, m/z 594 ($M^{+\bullet}$, 60%).

Anal. Calcd. for $C_{40}H_{26}N_4O_2 \cdot 1.5\ H_2O$: Found: C, 77.28; H, 4.70; N, 9.01. Found: C, 76.83; H, 4.51; N, 9.02.

^{13}C NMR Data of Ligands L_1-L_{12} in Deuterated 1,1,2,2-Tetrachloroethane (TCE). Chemical Shifts in ppm Downfield from Tetramethylsilane.

2,6-Bis(4'-phenyl-2'-quinolinyl)pyridine (**bpqpy**, L_1).

The following ^{13}C nmr resonances were observed: 155.6, 155.4, 148.7, 148.3, 138.2, 137.8, 130.1, 129.6, 129.4, 128.5, 128.3, 126.8, 126.5, 125.6, 122.2, 119.2.

2,6-Bis(4'-phenyl-2'-quinolinyl)benzene (**bpqb-H**, L_2).

The following ^{13}C nmr resonances were observed: 156.4,149.2, 148.6, 140.1, 138.0, 129.9, 129.6,129.5, 129.3, 128.7, 128.6, 128.4, 125.7, 126.6, 126.5, 125.6, 119.3.

2,6-Bis(6'-methyl-4'-phenyl-2'-quinolinyl)pyridine (**bmpqpy**, L_3).

The following ^{13}C nmr resonances were observed: 155.8, 155.7, 148.8, 148.7, 139.6, 138.7, 137.8, 129.7, 129.1, 129.0, 128.5, 128.2, 125.4, 124.8, 122.2, 118.6, 21.7.

2,6-Bis(6'-methyl-4'-phenyl-2'-quinolinyl)benzene (**bmpqb-H**, L_4).

The following ^{13}C nmr resonances were observed: 156.4, 148.9, 148.8, 140.2, 139.9, 138.2, 129.5, 129.2, 129.0, 128.7, 128.5, 128.4, 128.3, 126.5, 125.3, 123.7, 118.6, 21.7.

2,6-Bis(6'-nitro-4'-phenyl-2'-quinolinyl)pyridine (**bnpqpy**, L_5).

The following ^{13}C nmr resonances were observed: 154.6, 150.8, 149.9, 145.7, 134.4, 134.0, 131.8, 129.5, 129.3, 129.0, 128.18, 127.1, 124.7, 123.5, 122.9, 120.8.

2,6-Bis(6'-nitro-4'-phenyl-2'-quinolinyl)benzene (**bnpqb-H**, L_6).

The following ^{13}C nmr resonances were observed: 152.2, 151.3, 150.8, 145.3, 139.3, 136.5, 131.8, 129.9, 129.8, 129.4, 129.1, 127.2, 124.8, 124.4, 123.1, 122.9, 120.7.

2,6-Bis(6'-acetylamino-4'-phenyl-2'-quinolinyl)pyridine (**bapqpy**, L_7).

The following ^{13}C nmr resonances were observed: 161.7, 154.7, 151.5, 147.8, 145.9, 134.4, 131.8, 130.8, 129.5, 128.6, 127.8, 127.0, 125.6, 123.1, 119.8, 119.5, 113.2, 29.6.

2,6-Bis(6'-acetylamino-4'-phenyl-2'-quinolinyl)benzene (**bapqb-H**, L_8).

The following ^{13}C nmr resonances were observed: 162.3, 155.2, 154.2, 147.9, 143.9, 139.9, 139.0, 132.5, 130.7, 129.4, 128.7, 127.7, 126.1, 124.8, 122.5, 119.9, 119.5, 114.0, 29.6.

2,6-Bis(6'-bromo-4'-*p*-methoxyphenyl-2'-quinolinyl)pyridine (**bbpqpy**, L_9).

The following ^{13}C nmr resonances were observed: 159.9, 155.5, 155.2, 148.2, 146.7, 137.7, 132.8, 131.8, 130.9, 130.0, 129.0, 128.5, 127.9, 123.8, 120.1, 114.1, 55.5.

2,6-Bis(6'-bromo-4'-*p*-methoxyphenyl-2'-quinolinyl)benzene (**bbpqb-H**, L_{10}).

The following ^{13}C nmr resonances were observed: 159.9, 156.6, 148.4, 147.0, 139.6, 133.1, 131.6, 130.7, 129.6, 129.5, 128.8, 127.8, 127.1, 126.6, 120.5, 120.0, 114.3, 55.5.

2,6-Bis(6'-cyano-4'-*p*-methoxyphenyl-2'-quinolinyl)pyridine (**bcpqpy**, L_{11}).

The following ^{13}C nmr resonances were observed: 160.2, 154.6, 155.2,149.4, 138.2, 135.1, 132.4, 131.5, 130.9, 130.0, 129.0, 127.9, 126.3, 120.3, 119.1, 114.4, 114.3, 55.5.

2,6-Bis(6'-cyano-4'-phenyl-2'-quinolinyl)benzene (**bcpqb-H**, L_{12}).

The following ^{13}C nmr resonances were observed: 160.2. 158.8, 149.7, 149.6, 139.4, 132.4, 131.4, 130.8, 130.2, 129.6, 129.5, 128.7, 127.0, 125.5, 120.4, 114.5, 109.4, 55.5.

Acknowledgments.

This work was supported by the Ministero della Università e Ricerca Scientifica e Tecnologica, 60% funds.

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