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Synthesis of Bridging Electron Transfer Donor Ligands.

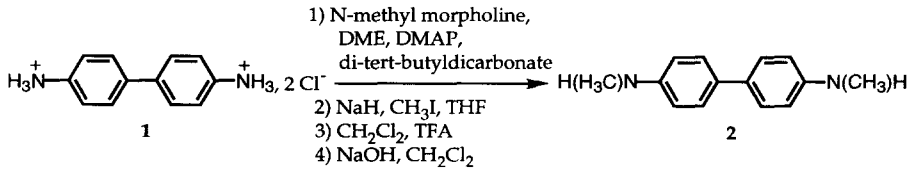
Sandrine Chodorowski-Kimmes, Thomas J. Meyer*
Department of Chemistry, The University of North Carolina, CB#3290,
Chapel Hill, North Carolina, 27599-3290, USA.

Abstract : The syntheses of three bridging electron transfer donor ligands are described based on coupling of the electron transfer donor, N, N'-dimethylbenzidine with two 2,2'-bipyridines. Two different coupling strategies are used : coupling between an acid and an amine with formation of an amide, and nucleophilic coupling between an amine and an electrophilic bipyridine.

Molecular systems have been designed that undergo intramolecular, photochemical electron and energy transfer and begin to mimic the redox splitting characteristics of the reaction center in photosynthesis. The metal-to-ligand-charge transfer (MLCT) excited state of polypiridyl complexes of ruthenium or osmium such as $[Ru(bpy)_3]^{2+}$(bpy is 2,2'-bipyridine) have been of particular importance in these studies[1]. Despite their extensive use in molecular assemblies, many fundamental issues regarding the photochemically induced single electron transfer reactions of these complexes with covalently attached quencher ligands remain unaddressed.

In this paper, we report the synthesis and electrochemical properties of a new family of bridging ligands which will allow us to link electron transfer donor to acceptor chromophores. These bridging ligands are designed to have redox potentials between those of the chromophore excited state and an ultimate donor. They are based on alkylated benzidines, with alkylation a requirement because of the instability of oxidized benzidines bearing dissociable protons.

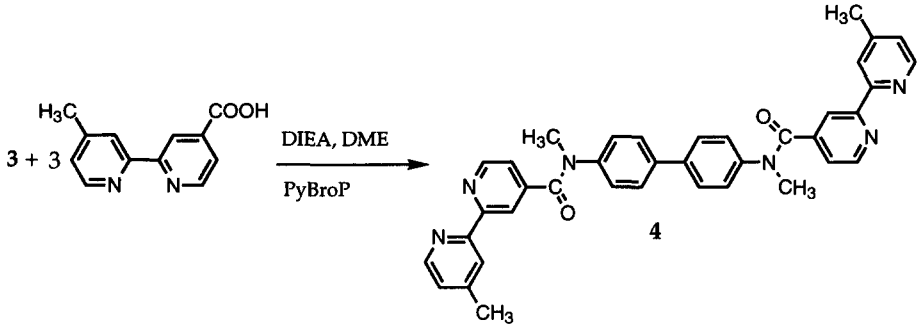
Synthesis of N,N'-dimethyl-benzidine (**2**) was achieved by first protecting benzidine (**1**) with di-tert-butyl dicarbonate (Boc), following by alkylation, and deprotection of the Boc group, eq. 1.



1 2 (1)

The Boc protection step (64%) was carried out in anhydrous ethylene glycol dimethyl ether (DME) under basic conditions (N-methyl-morpholine), in the presence of a catalyst (4-dimethylaminopyridine, DMAP). The reaction was performed under nitrogen, in the dark, at 55°C, for 40 hours. The yield in DMF was decreased to 30%. Alkylation of di-tert-butyl-benzidinecarbamate was achieved by modifying a known procedure.[2] To obtain complete di-alkylation of di-tert-butyl-benzidinecarbamate, sodium hydride and iodomethane were added in excess. The reaction was complete after two hours. No purification was required before the deprotection step. Deprotection was achieved by the addition of a mixture of trifluoroacetic acid (TFA) and CH_2Cl_2 (1:1, V:V) at room temperature. The acid salt of **2** was neutralized with 1M NaOH and precipitated in its acidic form by addition of gaseous HCl to ether solutions to give N,N'-dimethyldibenzidinium, $2Cl^-$ (**3**) in 70% yield.[3] The deprotonated form is unstable toward oxidation by the air.

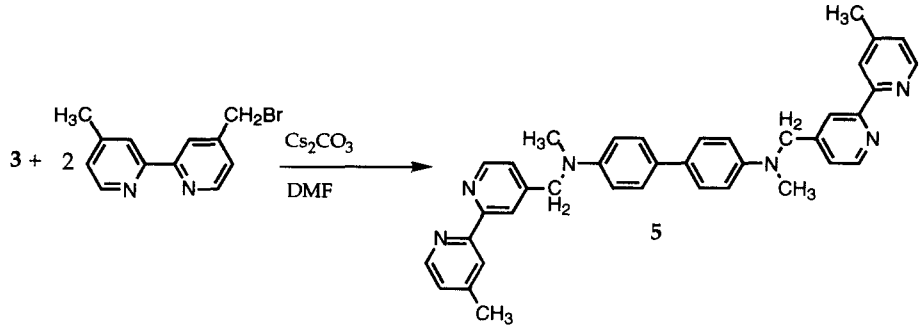
The chloride salt **3** was coupled with 4'-methyl-2,2'-bipyridine-4-carboxylic acid[4] in DME under basic conditions (N,N-diisopropylethylamine, DIEA) to form the amide. The coupling reagent was bromotripyrrolidinophosphonium hexafluorophospate (Py-BroP), eq. 2.



(2)

The coupling reaction was based on a literature procedure[5] and was conducted in the dark, under N_2, at room temperature over a 12 hour period. Ligand **4** was obtained after purification on alumina with a total yield of 70%.[6]

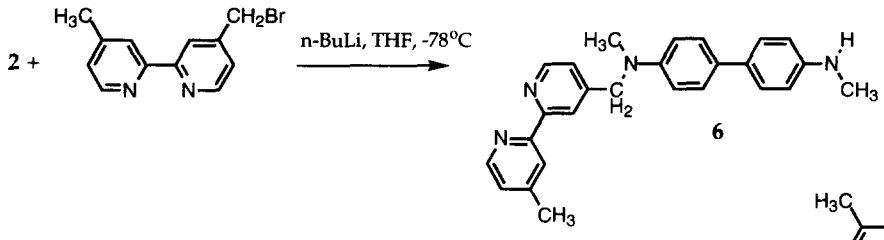
In order to increase the redox potential of the bridging ligand as a reductant we prepared two related ligands, one with one and one with two amine groups. Two different methods were used depending on the degree of benzidine substitution required. The bridging ligand with two amines was formed by coupling **3** with 4-bromomethyl-4'-methyl-2,2-bipyridine.[7] To a solution of DMF containing cesium carbonate were added **3** and 4-bromomethyl-4'-methyl-2,2-bipyridine, eq. 3.



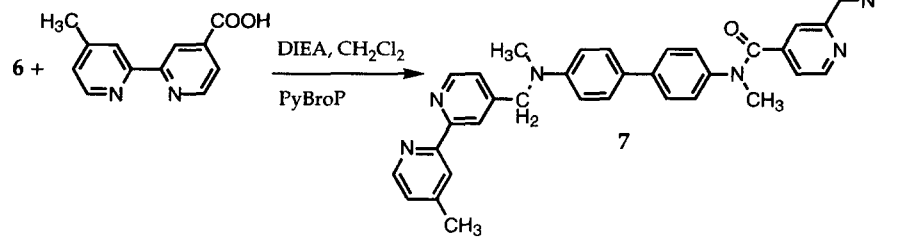
(3)

Cesium carbonate and 4-bromomethyl-4'-methyl-2,2-bipyridine were added in excess to the solution. The reaction was carried out in the dark under N_2, at room temperature for 24 hours. Ligand **5** was obtained in 70% yield.[8] Precautions were taken in purifying and storing this ligand due to its easy air oxidation.

The third ligand, containing a single amine group, was prepared in two steps. In the first step mono substitution of N,N'-dimethyl-benzidine by 4-bromomethyl-4'-methyl-2,2-bipyridine was affected with formation of **6**, eq.4. In the second step, amide bond formation occurred between 4'-methyl-2,2'-bipyridine-4-carboxylic acid and the free amine group of ligand **6**, eq. 5.



(4)



(5)

In the first step, one equivalent of n-butyl-lithium in hexane at -78°C was added to a solution of **2,** followed by addition of one equivalent of 4-bromomethyl-4'-methyl-2,2-bipyridine. This gave ligand **6** in 46 % yield.[9] The product was purified on silica with precautions taken to avoid air oxidation.

Bridging ligand **7** was obtained (80%)[10] after coupling **6** with 4'-methyl-2,2'-bipyridine-4-carboxylic acid by using PyBrop in CH_2Cl_2 under basic conditions (DIEA). The preparation of this ligand in the net sense involves two well-known coupling reactions and better yields were obtained by first introducing the amine function followed by formation of the amide.

The electron transfer donor power of these bridging ligands is defined by the reduction potentials for their $D^{+/0}$ couple. They are 0.54 V, 0.88 V and 1.54 V (vs the saturated calomel electrode (SCE) in CH_3CN, $\mu = 0.1$) for **5**, **7** and **4** respectively. This new sequence provides a family of polypyridyl bridging ligands with a gradient of redox potentials. We anticipate that they will play an important role in the design of molecular assemblies for photochemical energy conversion.

Acknowledgment

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References and Notes.

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2. Croce, P.D.; La Rosa, C.; Ritieni A. *J. Chem. Research (S)* **1988**, 346-347.
3. NMR data for **3** : NMR ^1H, 200 Mhz, (D_2O) : 7.59 (4H, d, J=8.6 Hz), 7.35(4H, d, J=8.5 Hz), 2.89 (s, 6H).
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6. ^1H NMR data for **4** : NMR ^1H, 200 Mhz, (CD_2Cl_2) : 8.44 (m, 4H), 8.37 (s, 2H), 8.16 (s, 2H), 7.38 (d, 4H, J=8.3Hz), 7.1 (m, 8H), 3.47 (s, $6H_{N\text{-}CH3}$), 2.4 (s, $6H_{CH3\text{-}bpy}$).
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8. ^1H NMR data for **5** : NMR ^1H, 200 Mhz, (CD_2Cl_2) : 8.55 (d, 2H, J=5.1 Hz), 8.48 (d, 2H, J=4.8 Hz), 8.33 (s, 2H), 8.27 (s, 2H), 7.39 (d, 4H, J=8.9Hz), 7.15 (m, 4H), 6.75 (d, 4H, J=8.9Hz), 4.62 (s, $4H_{CH2}$), 3.12 (s, $6H_{N\text{-}CH3}$), 2.42 (s, $6H_{CH3\text{-}bpy}$).
9. ^1H NMR data for **6** : NMR ^1H, 200 Mhz, ($CDCl_3$) : 8.59 (d, 2H, J=4.8 Hz), 8.52 (d, 2H,J=5.1 Hz), 8.33 (s, 2H), 8.23 (s, 2H), 7.40 (m, 4H), 7.20 (d, 2H, J=5.1 Hz), 7.13 (d, 2H, J=5.1 Hz), 6.76 (d, 4H, J=8.9Hz), 6.64 (d, 2H, J=8.6 Hz), 4.6 (s, $2H_{CH2}$), 3.6 (s,1 H), 3.09 (s, $3H_{N\text{-}CH2\text{-}bpy}$), 2.85 (s, $3H_{N\text{-}H}$), 2.42 (s, $3H_{CH3\text{-}bpy}$).
10. ^1H NMR data for **7** : NMR ^1H, 200 Mhz, ($CDCl_3$): 8.51 (m, 5H), 8.37 (s,1H), 8.25 (s, 1H), 8.07 (s, 1H), 7.35 (m, 4H), 7.13 (m, 6H), 6.70 (d, 2H, J=8.9Hz), 4.51 (s, 2H), 3.50 (s, 3H), 3.15 (s, 3H), 2.50 (s, 3H), 2.38 (s, 3H).

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