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The Use of a Monoorganotin Derivative of Pyrene in the Palladium(0)-Catalyzed Synthesis of a New Metal-Cation Complexing Molecule Displaying Excited State Charge Transfer Properties

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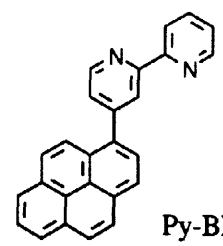
Abstract: The synthesis of ligand Py-BPY, in which the 1-pyrenyl group is directly connected to the 2,2'-bipyridyl unit, is described. Preliminary fluorescence results are indicative of the formation of an emitting intramolecular charge transfer state.

During the last decade, a great deal of theoretical and experimental work has been devoted to the study of molecules incorporating electron donor and acceptor subunits linked by a single σ-bond that display a fluorescence emission from highly polar charge transfer (CT) singlet states.[1-3] Beside their fundamental importance,[1,4] such fluorescent CT chromophores do represent attractive components for the conception of engeneered molecular and supramolecular systems performing diverse functions such as metal-cation recognition and detection,[5] interactions with DNA oligomers,[6] or molecular switching.[7]

In line with our investigations on fluorescent chemosensors for transition-metal ions,[8] we focused our attention on the design and the synthesis of light-sensitive complexing agents in which the pyrene chromophore and the 2,2'-dipyridyl (bpy) unit are connected by a single σ-bond. It occured to us that the prototype compound, 4-(1-pyrenyl)-2,2'-bipyridyl (Py-BPY), might (i) display intramolecular CT state emission, the pyrene moiety and the the bpy unit playing, respectively, the role of electron donor and acceptor,[9] and (ii) represent a versatile system to investigate the interplay between metal-ion complexation and CT state photophysical features. It is noteworthy that a number of fluorescent molecules has been reported in which the 1-pyrenyl group was shown to act either as electron donor[1,6,12] or acceptor[4,13,14].



Py-BPY

Critical to the synthesis of symmetrical and nonsymmetrical biaryl molecules is the use of efficient synthetic routes to perform C-C coupling reactions. Palladium(0)-catalyzed cross-coupling reactions have revealed among the most powerful methods, based on organotin or boronic-acid derivatives as precursors.[15,16] Recently, some of us reported[17] the high reactivity and the remarkable versatility of *pentacoordinated monoorganotin* reagents in coupling reactions with organic halides under Pd catalysis. These results prompted us to apply this synthetic method to the synthesis of compound Py-BPY (Scheme). The latter was readily obtained[18] in 61% isolated yield from 1-iodo-pyrene[19] and 4-bromo-2,2'-bipyridine[20],

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which demonstrated the synthetic potentiality of the monorganotin-reagent-based method in the case of pyridin derivatives as substrates. The 250-MHz ^{1}H NMR spectrum of Py-BPY in $CDCl_3$ is given in Figure 1. The connection of the 1-pyrenyl moiety to an aromatic group *via* a single bond has been already effected under the classical Stille and Suzuki coupling conditions. This required the tedious preparation of 1-pyrenyl(tributyl)stannane[6] and 1-pyrenylboronic acid[21] precursors, respectively, which involved a halogen-lithium exchange step between 1-bromopyrene and *tert*-butyllithium at low temperature. Here no such drastic conditions are required and the pentacoordinated tin intermediate is quantitatively generated *in situ* by reacting 1-iodopyrene with bis[N,N-bis(trimethylsilyl)amino]tin(II) in mild conditions (Scheme).[18] This method should be of great synthetic value for the elaboration of conjugated materials and photonic supramolecular systems. Moreover, it is environmentally friendly since the desired product is obtained free of organotin contamination.

Scheme

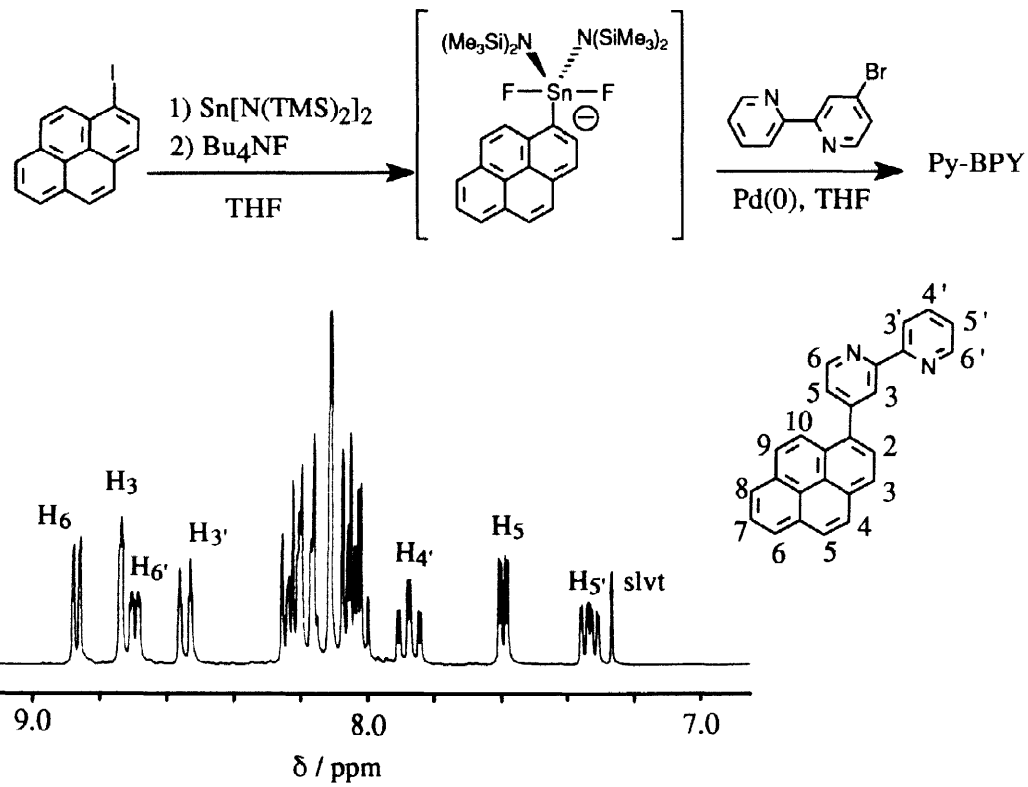

Figure 1. 250-MHz ^{1}H NMR spectrum of Py-BPY in $CDCl_3$ at room temperature. The assignement of the pyrene proton resonances is given in reference 18.

Room temperature absorption and fluorescence emission spectra of Py-BPY were recorded in four aprotic solvents of different polarity, and in the protic solvent methanol. The shape and the position of the first absorption band (λ_{max}=343 nm, ε_{max}=29800 M^{-1} cm^{-1}) were found to be independent of the solvent (Figure 2). On the contrary, increasing the solvent polarity induced a significant red-shift of the fluorescence maximum, along with the loss of vibrational structure. In methanol, whose polarity is close to that of acetonitrile, a larger value of the shift was noticed, which could be attributed to hydrogen-bond formation between the methanol and the bpy unit.[1,22] For all solvent, the fluorescence excitation spectra scanned at different emission wavelengths matched the absorption spectrum. Furthermore, the emission profile was found to be independent of the excitation wavelength upon excitation over the first absorption band. These

observations are in keeping with those previously reported[1,12] for compounds in which the pyrene is connected to an acceptor group, and are indicative of the formation of an emitting CT state stabilized in polar solvents relative to the (π,π^*) state of pyrene. The difference in fluorescence maximum between diethyl ether and acetonitrile is 1500 cm^{-1} for Py-BPY, which is lower than the value (2700 cm^{-1}) obtained[1] for 4'-(1-pyrenyl) acetophenone. This suggests a lower value of the excited dipole moment of the former relative to the latter, consistently with the more negative value of the reduction potential of bpy[9] as compared to acetophenone.[3a]

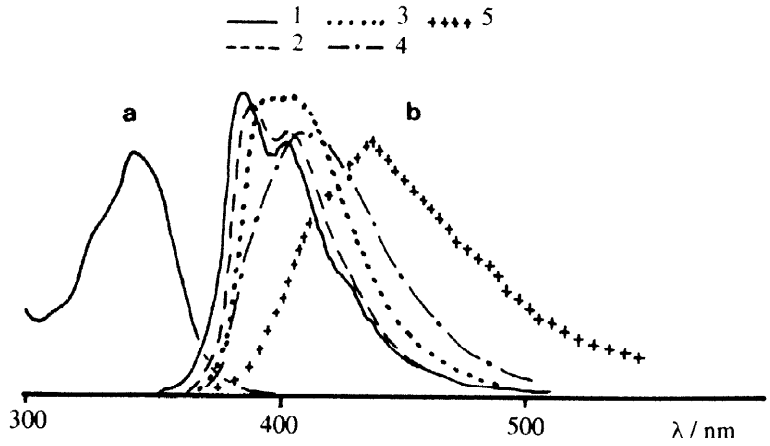

Figure 2. (a) First absorption band of Py-BPY (acetonitrile). (b) Corrected fluorescence emission spectra (RT, λ_{exc} = 342 nm) in: *n*-heptane (1, ν_{max} = 25970 cm^{-1}), diethylether (2, 25770cm^{-1}), tetrahydrofuran (3, 25060 cm^{-1}), acetonitrile (4, 24270 cm^{-1}), methanol (5, 22830 cm^{-1}).

The addition of an excess of trifluoroacetic acid to an acetonitrile solution of Py-BPY was followed by the quantitative quenching of the fluorescence emission and the appearance of a long-wavelength absorbing tail in the absorption spectrum. A similar behavior was noticed in the presence of an excess of $Zn(ClO_4)_2$. These observations are indicative of a strong charge-transfer interaction in both the ground and the excited states between the pyrene nucleus and the protonated (or complexed) bpy, due to the significant change of the reduction potential of bpy upon proton or metal-ion binding to the nitrogen atoms.[23] The photophysics of Py-BPY in the absence and in the presence of metal cations is being currently investigated, together with the preparation and the study of its photo- and redox-active coordination complexes with transition metal ions such as ruthenium(II).

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18. The synthesis of Py-BPY was performed following the typical procedure described in reference 17. The coupling step was carried out in THF (60 °C, 12 hours) using 2 mol% of dichlorobis (triphenylphosphine) palladium(II) as catalyst. Py-BPY was purified by chromatography on silica gel (CH_2Cl_2 - CH_2Cl_2/MeOH 90/10 v/v) and crystallization in methanol. Py-BPY: m.p.169 °C; 250-MHz ^{1}H NMR ($CDCl_3$) δ(ppm): pyrene resonances: 8.024 (H_7, dd, ^3J = 7.6 Hz), 8.03 (H_2, d, ^3J = 7.9 Hz), 8.05 (H_{10}, d, ^3J = 9.3 Hz), 8.11 (H_4, H_5), 8.17 (H_9, d, ^3J = 9.3 Hz), 8.18 (H_6, dd, ^3J = 7.6 Hz, ^4J =1 Hz), 8.21 (H_8, dd, ^3J = 7.6 Hz, ^4J =1 Hz), 8.23 (H_3, d, ^3J = 7.9 Hz); bpy resonances: 7.34 (1H, $H_{5'}$, ddd, ^3J = 8.0 Hz, ^3J = 4.8 Hz, ^4J =1 Hz), 7.59 (1H, H_5, dd, ^3J = 4.9 Hz, ^4J = 1.7 Hz), 7.87 (1H, $H_{4'}$, td, ^3J = 8.0 Hz, ^3J = 8.0 Hz, ^4J = 1.8 Hz), 8.54 (1H, $H_{3'}$, large-d, ^3J = 8.0 Hz), 8.69 (1H, $H_{6'}$, dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz), 8.73 (1H, H_3, d, ^4J = 1.7 Hz), 8.86 (1H, H_6, d, ^3J = 4.9 Hz). ^{13}C NMR ($CDCl_3$) δ (ppm): 156.5, 156.2, 150.3, 149.4, 149.2, 137.1, 134.8, 131.5, 131.0, 128.3, 128.1, 127.4, 127.2, 126.3, 125.7, 125.6, 125.3, 125.0, 124.8, 124.5, 123.9, 123.0, 121.5. EI-MS: m/z, 356.2 (M+). Anal. Calcd for $C_{26}H_{16}N_2$: C, 87.62; H, 4.52; N, 7.86. Found: C, 87.30; H, 4.62; N, 7.75.
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