Electronic Supplementary Information for Dalton Transactions

Supplementary Information

An Inconvenient Influence of Iridium(III) Isomer on OLED Efficiency

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Computational details:

The geometries N984 and N984b complexes were optimized by DFT calculations using the PBE0 exchange-correlation functional,[1] together with the cc-pvDZ basis set for N, C, O, H and the sdd basis set for Ir with related Stuttgart/Dresden effective core potentials as implemented in the Gaussian 03 (G03) program package.[2] The ground state geometry of both complexes were optimized with no symmetry constraints in vacuo, and the geometry of the lowest excited state was evaluated by optimizing imposing a triplet spin multiplicity, the triplet excited state being related to the emission process. On the ground state optimized geometries we performed frequency calculations at the same level of calculations employed for geometry optimization, finding all positive frequencies in confirmation that the optimized structure is a true minimum. We analyzed the electronic structure of ground and lowest state geometries in acetonitrile solution including the solvation effects by means of the PCM solvation model,[3] as implemented in the G03 program package. For both isomers we performed TDDFT calculations at the PBE0//cc-pvDZ;sdd level of theory in acetonitrile solution. Calculation of the lowest 70 singlet-singlet (S) excitations at the ground state optimized geometries allowed us to simulate a large (up to 210 nm) portion of the absorption spectrum. The simulation of the absorption spectra has been performed by a gaussian convolution with FWHM=0.5 eV. Moreover, we calculated at the ground state geometries the three lowest singlet-triplet (T) excitations, while at the triplet optimized geometries the three lowest singlet-singlet and singlet-triplet TDDFT excitations in acetonitrile. It has to be

noticed that the singlet-triplet excitations oscillator strengths are set to zero due to the neglect of spin-orbit coupling in the TDDTF calculations as implemented in G03.

References:

[1] Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, 110, 6158.

[2] Gaussian 03, Revision B05, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. *Gaussian, Inc.: Pittsburgh PA* **2003**.

[3] Cossi,M.; Rega,N.;Scalmani,G.; Barone,V. *J. Comp. Chem.* **2003**, *24*, 669.

Table S1: Lowest singlet-singlet (S) and singlet-triplet (T) excitation energies (nm; eV) and composition in terms of molecular orbital excitations for **N984** and **N984b** calculated at the singlet and triplet state optimized geometries. In parentheses the oscillator strengths of the singlet-singlet transitions are reported. Experimental values of the emission maxima (nm; eV) are reported for comparison.

	Em.(exp)	S_1	S_2	S_3	T_1	T_2	T_3
N984(S)	520; 2.387	401; 3.097 (0.07) H→L	388; 3.196 (0.00) H→L+1	356; 3.481 (0.01) H→L+2	459; 2.701 - H→L	451; 2.749 - H→L+1	393; 3.155 - H→L H-2→L
N984(T)		462; 2.683 (0.08) H→L	410; 3.026 (0.02) H→L+1	373; 3.324 (0.00) H→L+2	558; 2.222 - H→L	464; 2.675 - H→L+1	431; 2.877 - H-1→L H-3→L
N984b(S)	520; 2.387	387; 3.201 (0.03) H→L	371; 3.346 (0.02) H→L+1	361; 3.432 (0.09) H-1→L	458; 2.709 - H→L	444; 2.795 - H-1→L H-1→L+1	399; 3.107 - H-2→L+2 H-2→L
N984b(T)		437; 2.838 (0.07) H→L	383; 3.240 (0.02) H→L+1	380; 3.261 (0.103) H-1→L	561; 2.212 - H→L	442; 2.804 - H-1→L+1 H-1→L	426; 2.908 - H-3→L H-1→L

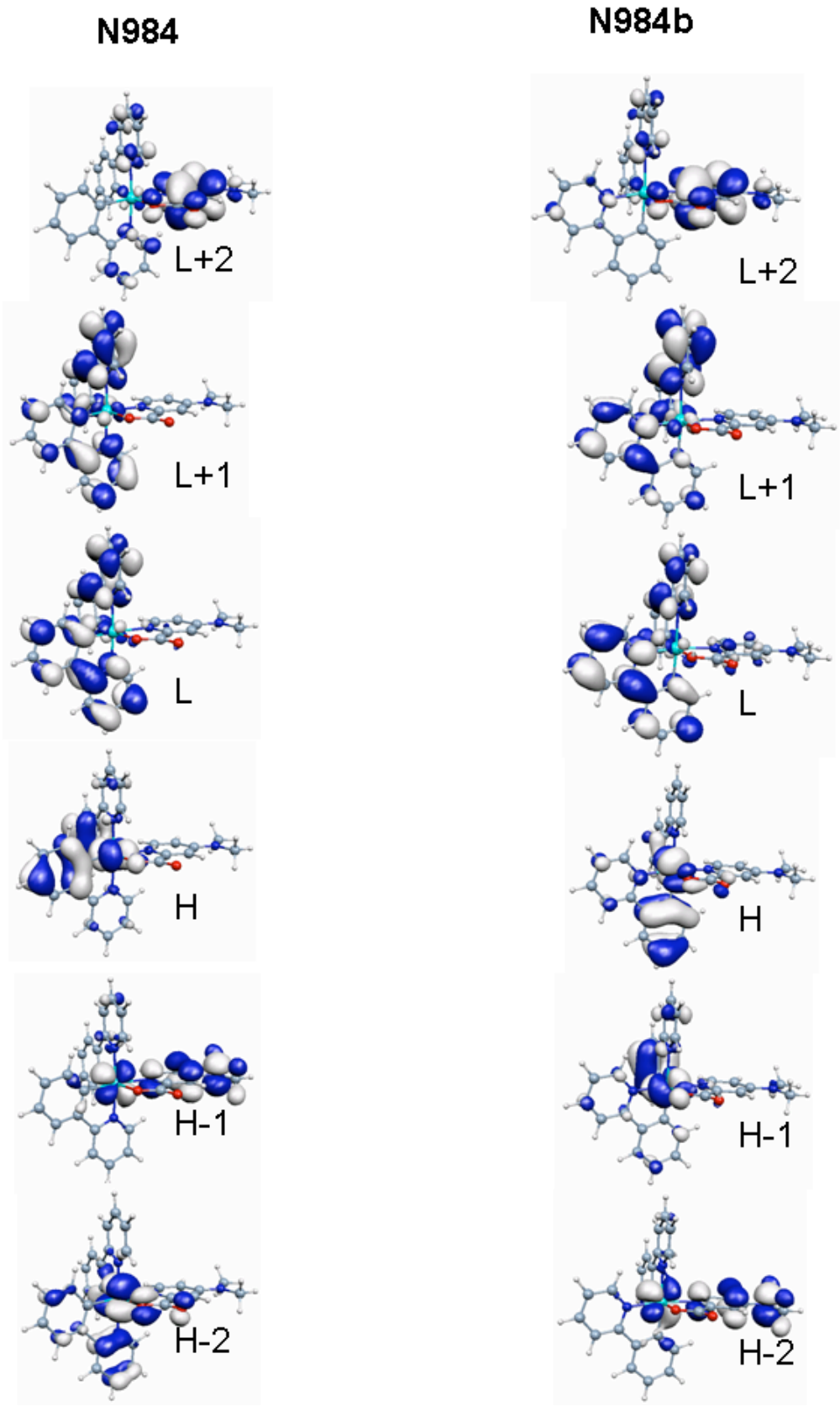


Figure S1. Molecular orbitals for N984 and N984b.

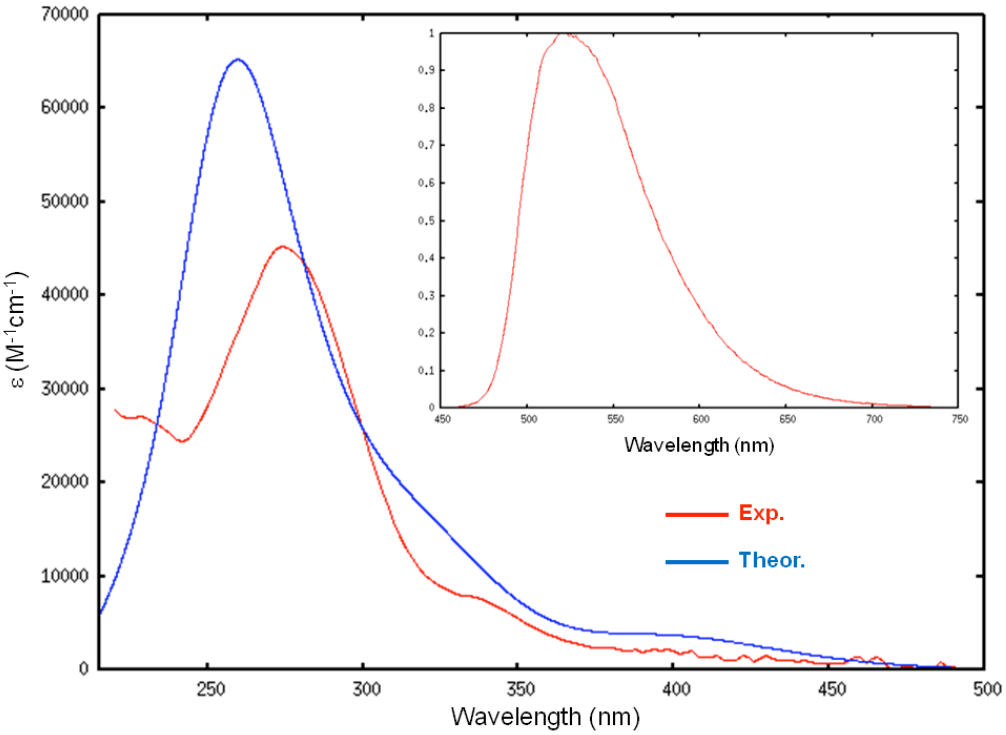


Figure S2. Comparison between the experimental (red) and calculated (blue) absorption spectra of N984 . The inset shows the experimental emission spectrum of N984.

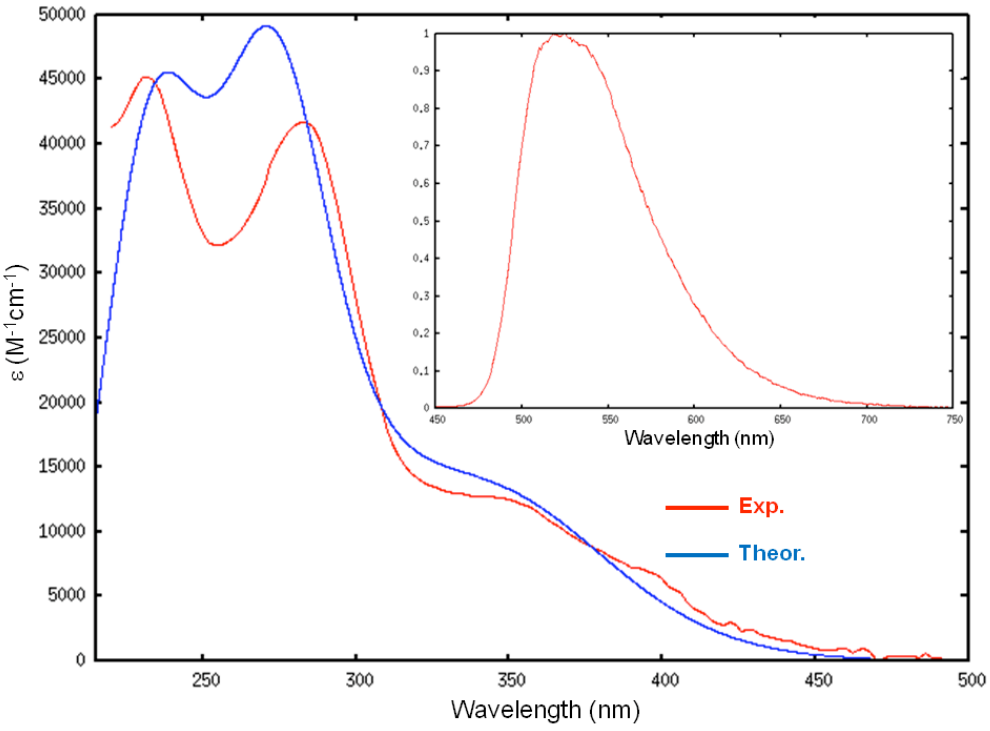


Figure S3. Comparison between the experimental (red) and calculated (blue) absorption spectra of N984b . The inset shows the experimental emission spectrum of N984b.

Assignment of the absorption spectra:

The N984 computed absorption spectrum shows a transition at 400 nm (f= 0.07) of H→L character. The H is a combination of Ir (t_{2g}) d_{xy} and π orbital on both the phenyl rings of the phenylpyridine ligands, while the L is a π* orbital completely delocalized on the phenylpyridine ligands. We therefore assign this transition as a MLCT one with a partial π – π* character. The experimental shoulder at ca. 340 nm is the result of transitions ranging from ca. 310-330 nm, the most intense is computed at 326 nm (f=0.13) and involves as starting states H-1 and H-2 and as arriving states L and L+1. The H-1 is a combination of the Ir (t_{2g}) d_{xz} orbital with a π orbital delocalized on the dimethylaminopyridine, while the H-2 shows the antibonding π combination of the Ir (t_{2g}) d_{yz} orbital with the p orbitals on the Ir adjacent oxygen and one nitrogen. The L+1 is a π* orbitals, entirely delocalized on the phenylpyridine ligands, degenerate with the L. We therefore assigned the computed transition at 326 nm as a mixed MLCT and π –π* transition, which differ from the lowest energy transition for the partial charge-transfer character of the transition from the dimethylaminopyridine ligand to the phenylpyridine ones.

Conversely to N984 case, the computed absorption spectrum of N984b shows a structured absorption band in the range 310-390 nm. The lowest energy transition is at 387 nm (f=0.03) and involves the H as starting state and the L and L+1 as arriving state. The H is very similar to that of N984 complex, showing contribution from the Ir (t_{2g}) d_{yz} and the π orbital on both the phenyl rings of the phenylpyridine ligands, even though the charge is delocalized on a different plane. L and L+1 are a couple of almost degenerate orbitals, essentially delocalized on both the phenylpyridine ligands. The most significant transitions composing the low energy absorption band are computed at: 361 nm (f=0.09), 349 nm (f=0.05), 327 nm f=0.05, 324 nm f=0.04 and 316 nm (f=0.08). Both transitions at 361 and 349 nm are from the H-1 to L and L+1, respectively. The H-1 shows a delocalization similar to that of H-2 of N984, even though again with a different symmetry, combaining the Ir (t_{2g}) d_{xy} with the p orbitals on the trans oxygen and nitrogen atoms. Therefore these transitions have a similar mixed MLCT/π – π* character within the phenylpyridine ligands.

The transitions 327, 324 and 316 nm involve the H-2, which is similar to the N984 H-1, showing contribution from the Ir t_{2g} (d_{yz}) orbital and the N and C p orbitals of the dimethylaminopyridine moiety.

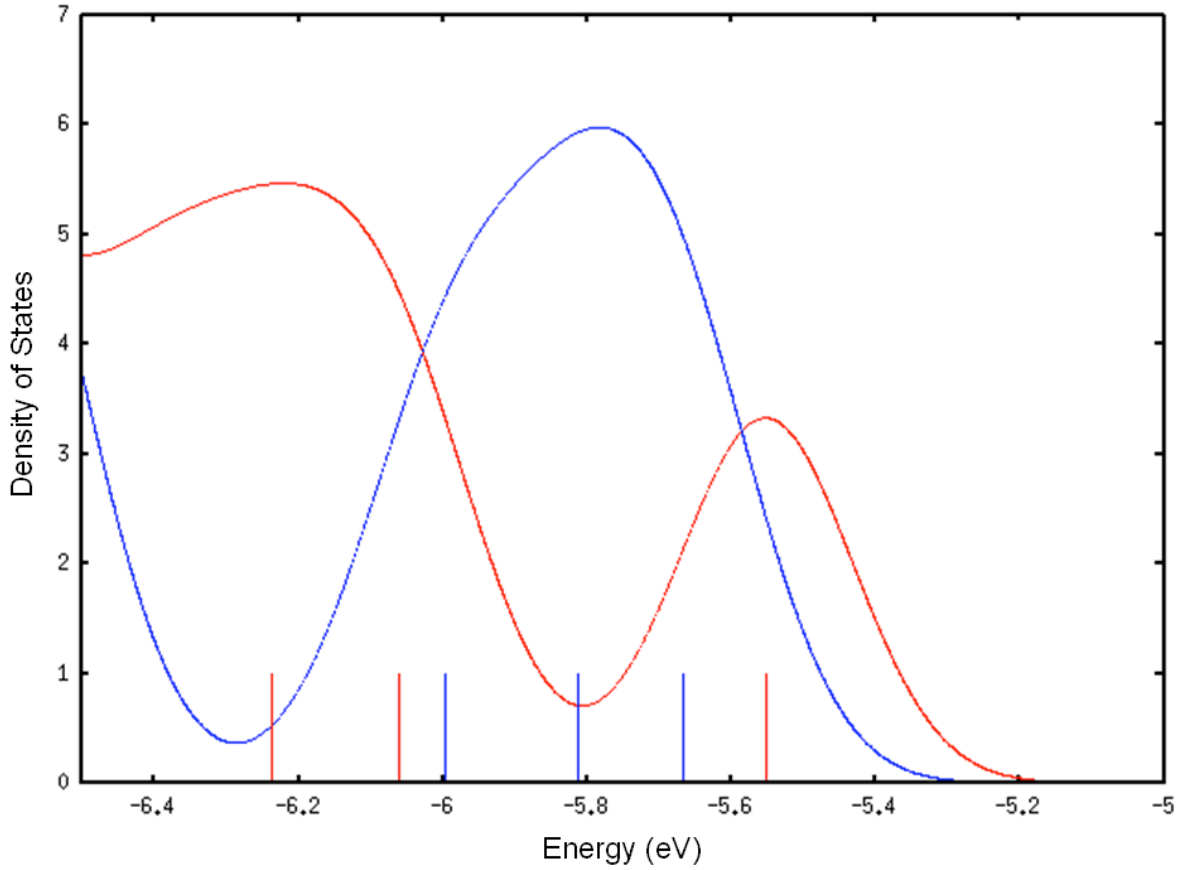
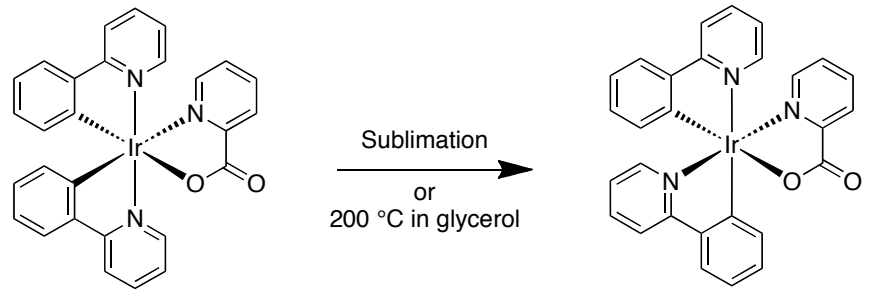


Figure S4. Calculated density of occupied states for N984 (red) and N984b (blue). The vertical lines represent the calculated orbital energies (eV).

The HOMO of N984 and N984b are calculated at -5.55 and -5.67 eV, respectively. These values are only slightly more negative than the experimental oxidation potentials for N984 and N984b, which are found at -5.35 and -5.37 V vs. Vacuum, respectively. These values were calculated by adding -4.84 V to the measured oxidation potentials vs. Fc/Fc+. By rescaling the calculated values to match with the experimental oxidation potentials, i.e. shifting the calculated values by +0.2 eV, we notice that the density of occupied states for N984b partly overlaps with the PVK energy level, which is commonly located at -5.8 V. On the other hand, the N984 density of states does not overlap with the hole conductor level, therefore N984 acts as a hole trap.

Isomerization of $Ir(ppy)_2(pic)$



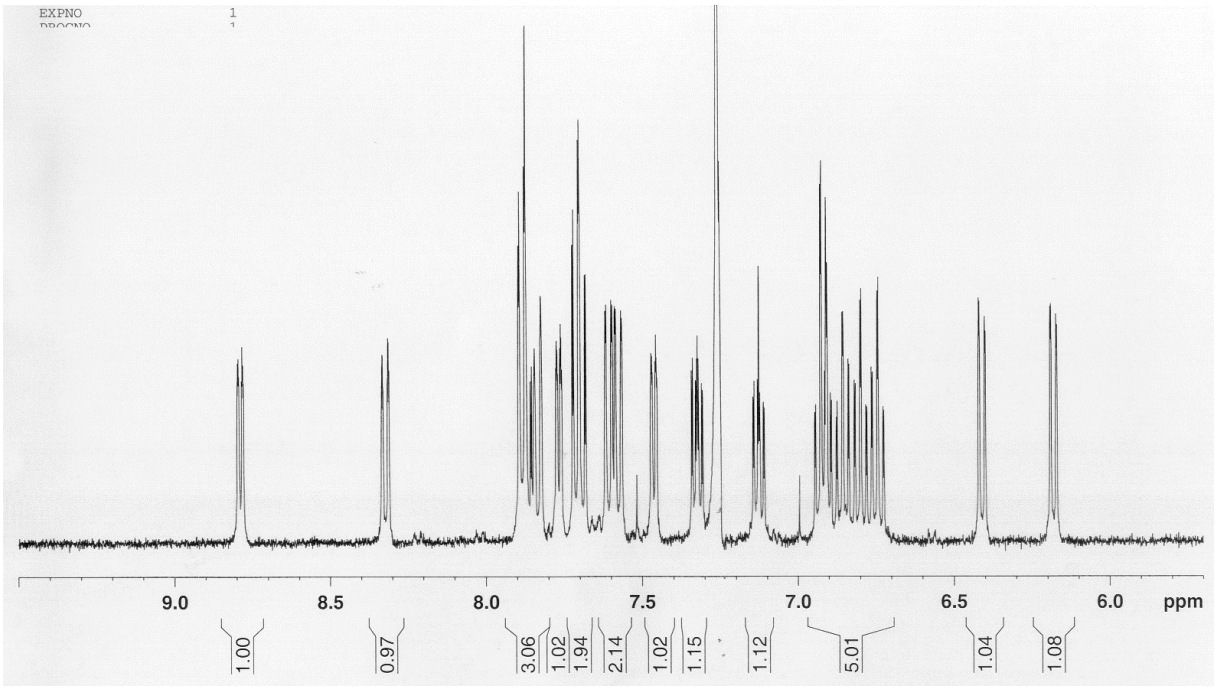
pure *meridional*-$Ir(ppy)_2(pic)$

mixture of complexes
likely containing the *cis-mer* isomer

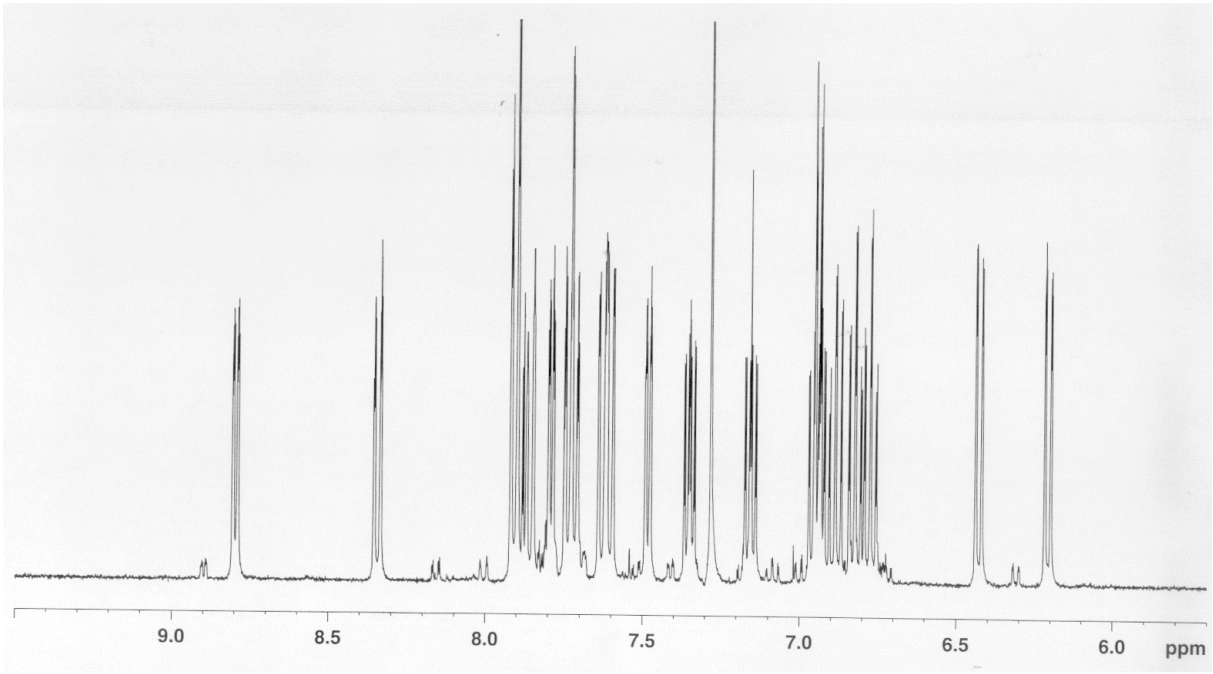
Reaction in glycerol : 48 mg of $Ir(ppy)_2(pic)$ was suspended in 30 mL of glycerol. The mixture was heated at 80 °C under strong argon bubbling for one hour. Then the mixture was heated at 205 °C for 15 hours under argon and protected from light with aluminium foil. The yellow solution was cooled down to room temperature and water was added to induce precipitation and the crude was filtered, washed with water and dried. The solid was directly used for ^1H NMR.

Subimation: Gradient sublimation at a pressure of about10^{-5} mbar as for N984.

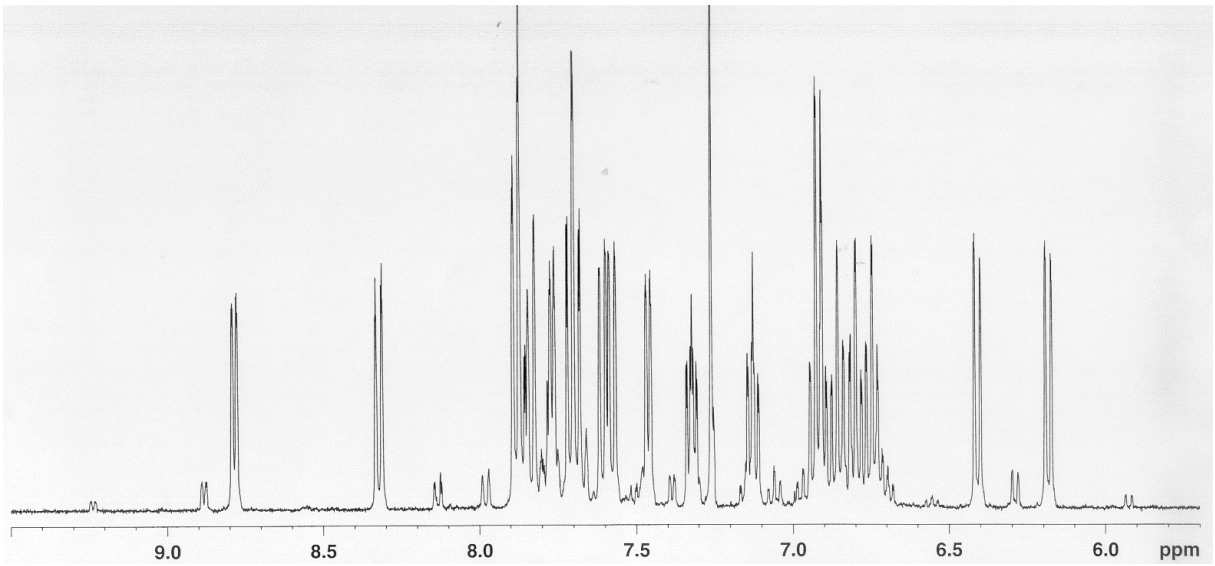
^1H NMR of $Ir(ppy)_2(pic)$ in $CDCl_3$



^{1}H NMR in $CDCl_3$ of the crude reaction in glycerol



^{1}H NMR in $CDCl_3$ of the sublimed product



In both case, new set of signals appears. The characteristic doublet at 8.9 ppm is similarly observed in isomerization of N984 and FIrPic and is attributed to the cis-mer isomer. Therefore, while the dimethyl amino group may favour the isomerization process, it is apparently not a requirement for isomerization to occur.