

8-HYDROXYQUINOLINE AND FUNCTIONALIZED INDOLE IN ZINC COMPLEXES: HYPOTHETICAL APPLICATION IN PHOTOPHYSICAL DEVICES

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This research project concerns the synthesis of functionalized indolic compounds for the construction of new zinc complexes, which are useful for a hypothetical application in photophysical devices. The syntheses that can be used to create these functionalized heterocycle compounds concern the use of two azoalkene molecules, thus exploiting a cyclization [4+2] or using the Attanasio O.A. synthesis [1]; in these cases, by using conjugate systems C = C and N = N, the obtained pyrrole will have a NHR group bound on the heteroatom. In this case, functionalization in C2 will also be important.

If the Hantzsch synthesis is used instead [2], the nitrogen of pyrrole binds a hydrogen. Therefore, the obtained indole will be functionalized in C2 and C3.

The indole thus obtained will be used in place of benzoic acid-ortho-amino acid (oABA) for the construction of zinc complexes; in fact, oABA presents two groups that can potentially bind zinc: oxygen from OH group of carboxylic acid and nitrogen from NH₂.

Similarly, we can make indolic compounds by taking into consideration the presence of these two groups in order to hypothetically exploit them in photophysical devices.

Several Zinc-based chelates with organic ligands have been synthesized for photophysical study [3] and for applications of light-emitting devices [4]. Among these chelates there are the Zn-based complexes with 8-hydroxyquinoline and substituted ligands of 8-hydroxyquinoline, due to their ability to emit light and transport electrons. Furthermore, quinolates of aluminium (Alq₂), lithium (Liq₂) and magnesium (Mgq₂) exhibit efficient luminescence in blue green region and find applications as emission layer in OLEDs [4]

In 2004 Wang [5] used functionalized polystyrene containing the 8-hydroxyquinoline nucleus (PST-CH₂-Q) to prepare a mixed zinc complex. The complex was then characterized with NMR ¹H and fluorescence techniques.

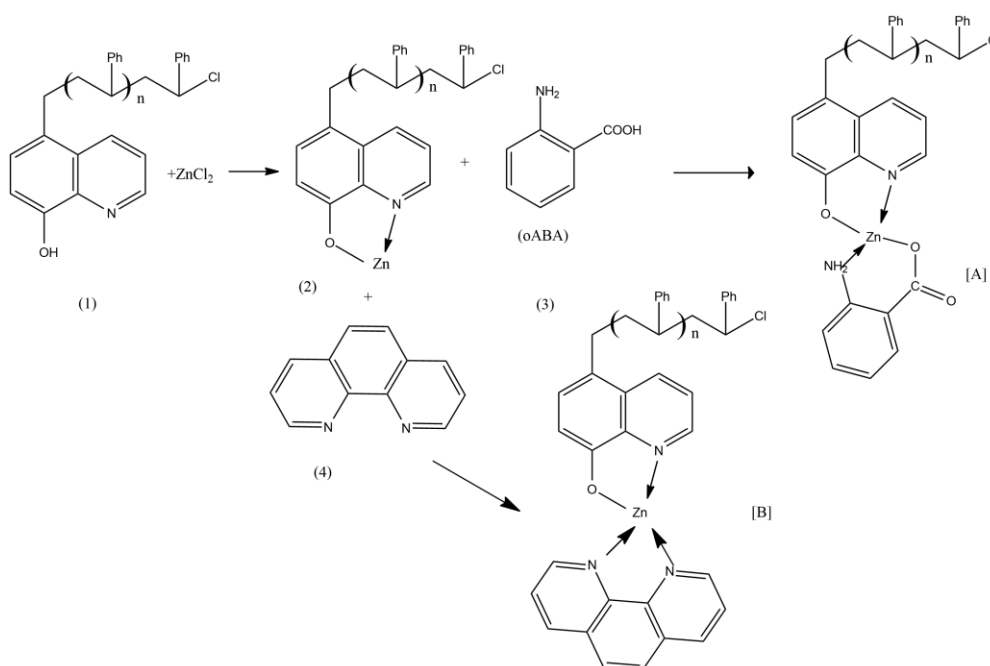


Figure 1

The PST-CH₂-Q compound was dissolved in DMF and was slowly added in a large amount of DMF solution ZnCl₂. O-aminobenzoic acid (oABA) was dissolved in DMF and gradually added to the DMF solution of PST-CH₂-Q-Zn; the mixed solution was mixed for about 10 hours and precipitated into a large amount of methanol. The insoluble product was washed with methanol and collected by filtration and dried under vacuum. The mixed PSt-CH₂-Q Zn (II) complex of oABA [A] was obtained. The same procedure was used when adding phenantropin, obtaining thus the compound [B].

Figure 1 shows that both oxygen and nitrogen from the 8-hydroxyquinoline nucleus of the molecule (2) participate in the binding to the zinc. By adding the compound (3), nitrogen of NH₂ and oxygen of OH of the carboxyl group participate in the binding with the zinc. Same thing when using phenantropin (4), in which there are two nitrogens that bind zinc. All of this was confirmed by NMR ¹H and fluorescence spectra.

Zinc then binds either to nitrogen with free electrons or to oxygen. Based on that, instead of oABA we can try to use a heterocycle, like the pyrrole that has at least two groups such as NHR or NH and OH to build new zinc complexes (**Figure 2**).



Figure 2

Heterocycle (5) can be obtained by using a cyclization [4+2] of two azoalkenes or by exploiting the 1998 reaction of Attanasi O.A. et al. ^[1] (**Figure 3**), while molecule(6), that presents substitutions in C2 and C3, can be obtained by using the Hantzsch synthesis ^[2] (**Figure 4**).

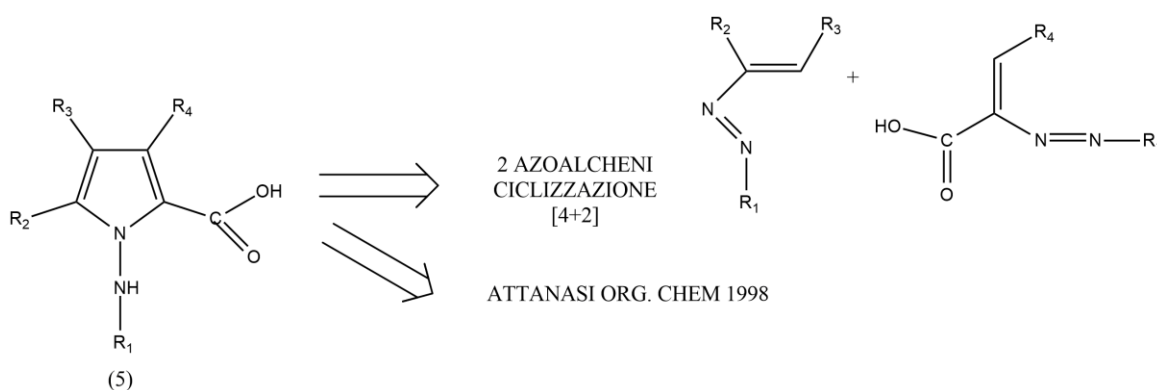


Figure 3

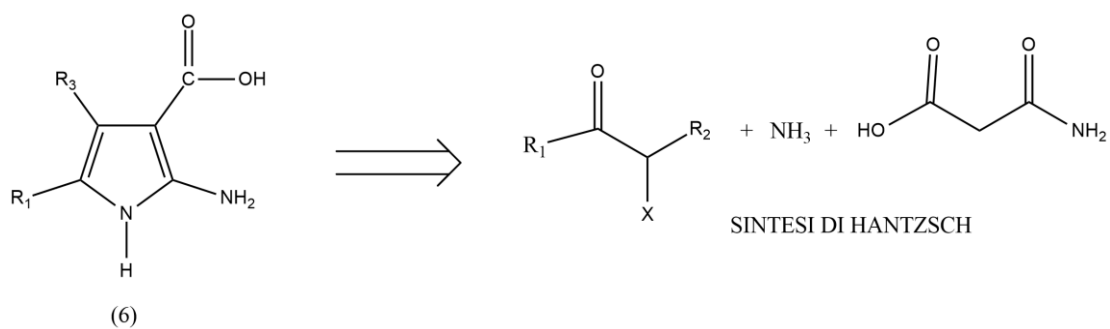


Figure 4

Hence the hypothesized complexes are the following, as shown in **Figure 5**.

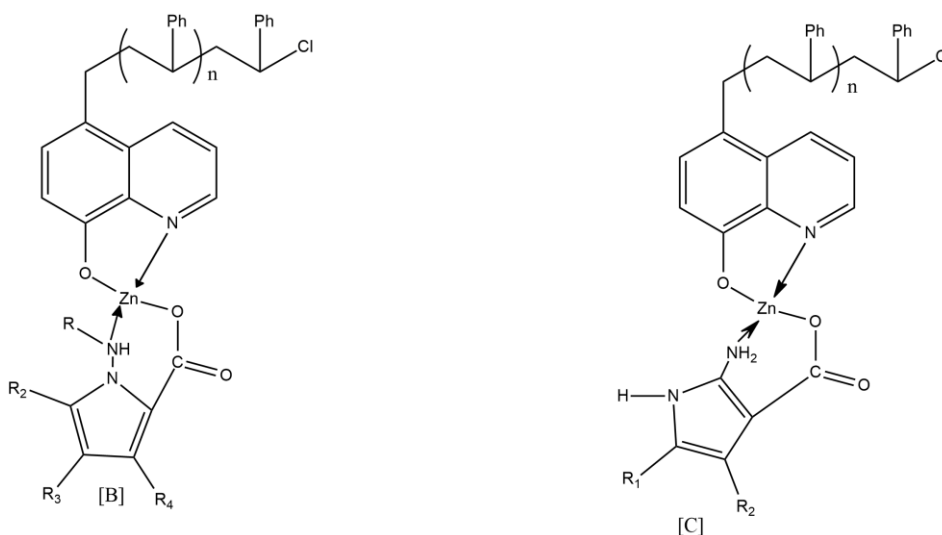


Figure 5

The decision to obtain the two types of indoles (5) and (6) arises from the fact that the binding distance between the atoms of N and O participating in the bond with the metal is 4 as in the compound (3) or O-aminobenzoic acid. This hypothesis will have to be verified through NMR ^1H spectra and fluorescence spectra and if the structures [B] and [C] are confirmed, it will be of interest to understand whether there could be any advantages in obtaining zinc complexes with functionalized indoli and whether they can also be used in photophysical devices.

Bibliography

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