NEW ELECTRORELEASING LIGANDS FOR THE PHOTOSENSITISATION OF RUTHENIUM

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1 Introduction

Our target is to prepare new bpy and ipy ligands having stronger electroreleasing behavior in order to induce improved photophysical properties in Ruthenium complexes.

“Pull”
On one side, carboxylic acids offer the ability to link to a surface like TiO,

“Push”
On the other side, electron donating groups can promote a shift of electron.

2 Pathway

Our retrosynthetic approach involves reusable mono- or difunctional pyridine systems.

3 Starting patterns

Previous works:

Works carried out in the lab on the 4-DMAP yielded efficient electroreleasing ligands.


How could we leverage this?

With the use of two patterns bearing either a conjugated or a saturated system both having a strong electroreleasing property according to the calculations.

4 Building blocks

The setup of new regioselective lithiation methods using the aggregated system BuLi-LiDMAE led to functionalised building blocks.

5 Assembly

Chlorine or tin precursors have been combined into coupling reactions to obtain new ligands demonstrating an increasing electroreleasing scale.

6 Homoleptic complexes

Only microwave assisted synthesis allowed us to prepare very quickly the corresponding homoleptic complexes from RuCl

7 Heteroleptic complexes

Again, the fast preparation of the dichlorinated intermediate complex could only be achieved through microwave irradiation.

Then the heteroleptic can be obtained with further treatment with dcbpy in an acetic acid / water mix.

8 Properties

<table>
<thead>
<tr>
<th>Light absorption</th>
<th>Light emission</th>
<th>Oxidation potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</td>
<td>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</td>
<td>E&lt;sub&gt;ox&lt;/sub&gt; (V vs. SCE)</td>
</tr>
<tr>
<td>465 (8600)</td>
<td>650</td>
<td>+1.16</td>
</tr>
<tr>
<td>480 (22000)</td>
<td>630</td>
<td>+1.12</td>
</tr>
<tr>
<td>495 (38500)</td>
<td>n.d.</td>
<td>+1.18</td>
</tr>
<tr>
<td>481 (12505)</td>
<td>n.d.</td>
<td>+0.17</td>
</tr>
<tr>
<td>520 (13176)</td>
<td>n.d.</td>
<td>-0.21</td>
</tr>
<tr>
<td>501 (15010)</td>
<td>n.d.</td>
<td>+0.20</td>
</tr>
</tbody>
</table>

As expected, the complexes show off excellent photophysical properties.

The low oxidation potentials obtained make them good competitors for photovoltaic use.

9 Conclusion

A first difficulty was to perform coupling reactions before the precursors get reduced. However, we were able to overcome that using chlorine and tin compounds in Stille reaction where other well-known coupling reactions failed.

A second difficulty was to prepare the complexes. Indeed, procedures described in the literature were unable to give access to the expected complexes.

However, we succeeded in setting up less time-consuming microwave assisted syntheses.

We now aim to synthesize original structures, still with electroreleasing groups, but with spacers between them and pyridine rings.