

# Enabling fluorescence sensing of methyl trialkylammonium chloride salts by functionalization of a calix[4]pyrrole with a Pt(II) cyclometallated compound

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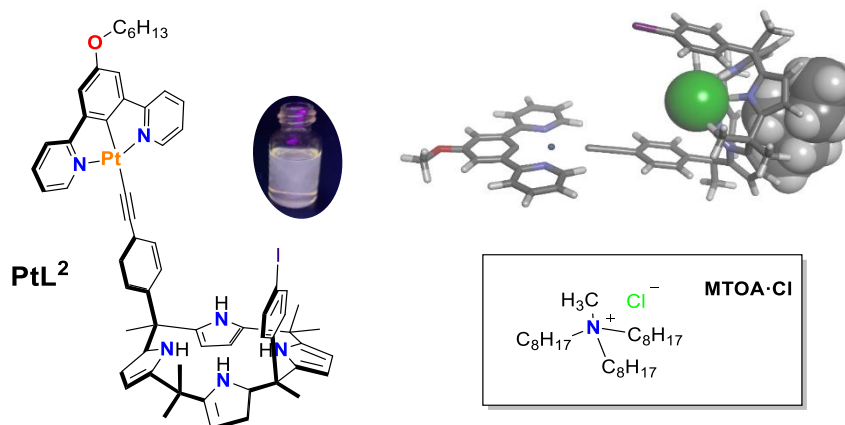
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Several examples of emissive C[4]Ps are described in literature as efficient anion receptors. The methods used to prepare them usually involved the covalent attachment of an organic fluorophore to the receptors' scaffold.<sup>1,2</sup> To the best of our knowledge, the use of emissive Pt(II) organometallic units for the construction of phosphorescent C[4]P sensors is unprecedented. Their significance lies in the phosphorescence emission exhibited by the receptors. Unlike typical organic luminophores that emit fluorescence, these emitters boast prolonged emission lifetimes and emit at longer wavelengths. Platinum(II) cyclometallated compounds, especially those derived from 1,3-dipyridilbenzene and containing acetylide ancillary ligands are known to present enhanced phosphorescence due to these strong field ligands minimizing the compound's non-radiative d-d transitions.<sup>3</sup>

Herein, we describe the synthesis of a highly emissive “two wall”  $\alpha,\alpha$ -isomer aryl-extended C[4]P, PtL<sup>2</sup>, bearing one cyclometallated Pt(II)-N<sup>c</sup>N-2,2'-[5-hexyloxy-1,3-phenylene] dipyridine unit inserted at the para-ethynyl residue of one of its meso-phenyl substituents (*Figure 1*, left). We characterize the binding properties of the mononuclear Pt(II) C[4]P receptor, PtL<sup>2</sup>, in solution, towards methyl trialkyl ammonium chloride salts by means of <sup>1</sup>H NMR titrations and isothermal calorimetry (ITC) experiments. The obtained results demonstrate the formation of a thermodynamically and kinetically highly stable 1:1:1 ion-paired complex, Cl<sup>-</sup> ⊂ PtL<sup>2</sup>•MTOA, featuring receptor separated binding geometry (*Figure 1*, right). The mononuclear PtL<sup>2</sup> receptor exhibits a slightly reduced binding affinity for the MTOA•Cl salt compared to the parent C[4]P. The binding of the chloride salt can also be monitored by luminescence titrations providing an advantage to PtL<sup>2</sup> in terms of sensitivity and ability to operate in intensity as well as in lifetime modes.



**Figure 1.** Chemical structure of the platinum(II) receptor PtL<sup>2</sup> and luminescence under UV-light (left) and energy minimized structure of Cl<sup>-</sup> ⊂ PtL<sup>2</sup>•MTOA.

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