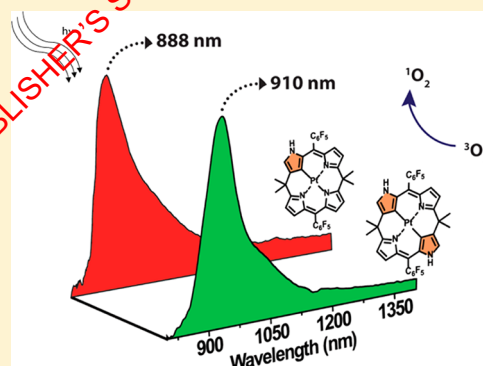


## Singly and Doubly N-Confused Calix[4]phyrin Organoplatinum(II) Complexes as Near-IR Triplet Sensitizers

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## Supporting Information

**ABSTRACT:** Organoplatinum(II) complexes of calix[4]phyrin analogues, singly N-confused calix[4]phyrin (Pt-2), and doubly N-confused calix[4]phyrin (Pt-3), were synthesized and characterized. The explicit structures of these organoplatinum(II) complexes were elucidated by single-crystal X-ray diffraction and spectroscopic studies. The introduction of N-confused pyrrole rings to the parent calix[4]phyrin scaffold was found to have profound effects on the photophysical properties, such as the bathochromic shifts of both the absorption and phosphorescence maxima. The triplet excited state properties of these platinum complexes were analyzed by DFT calculations at the B3LYP level. The organoplatinum(II) complexes derived from the deformed scaffolds can serve as potent triplet sensitizers for singlet oxygen generation under aerobic conditions.



## INTRODUCTION

Triplet sensitizers have garnered considerable attention owing to their potential applications in electroluminescence,<sup>1</sup> phosphorescence bioimaging,<sup>2</sup> and photocatalysis.<sup>3</sup> The corresponding triplet states formed via intersystem crossing (ISC) upon photoexcitation play an important role in photodynamic therapy<sup>4</sup> and oxygen sensing,<sup>5</sup> since the triplet energy transfer to the molecular oxygen (<sup>3</sup>O<sub>2</sub>) is the key process for the generation of singlet oxygen (<sup>1</sup>O<sub>2</sub>).<sup>6</sup> It would be a general approach that the heavy-atom effect of the spin–orbit coupling for 4d or 5d metals, such as Ir<sup>III</sup>, Pt<sup>II</sup>, Ru<sup>II</sup>, Os<sup>II</sup>, etc., allows efficient ISC to the triplet manifold.<sup>7</sup> Therefore, several transition-metal complexes have been regarded as efficient <sup>1</sup>O<sub>2</sub> generators that are capable of energy transfer to molecular oxygen.<sup>8</sup>

Among these photosensitizers, square-planar platinum(II) complexes are one of the promising species, especially for phosphorescence emitters as well as singlet oxygen sensitizers.<sup>9</sup> The most successful examples, such as porphyrin-based d<sup>8</sup> platinum(II) complexes, demonstrated high luminescence beyond the far-red region, and the triplet energies can be tuned by the levels of the molecular orbitals (i.e., HOMO and LUMO).<sup>10,11</sup> To date, many synthetic chemists have devoted great efforts to extend the energy of the triplet states for the sensitizers to the near-infrared (NIR) region through ligand

modifications (e.g., peripheral  $\pi$  extensions and core expansion with more than 18 $\pi$  conjugated scaffolds) (Figure 1).<sup>12</sup> However, when the  $\pi$ -conjugation of the ligand moieties was increased, the low solubility and chemical instability of the resulting derivatives hampered their practical use as photosensitizers. Therefore, the development of new types of ligand platforms for the platinum-based triplet sensitizers has been in demand, and a detailed study of the structure–property relationship for the photoluminescence and singlet oxygen generation efficiency is required.

In this context, we introduce a new approach whereby the triplet state energy (wavelength) can be tailored by the ligand modification on the basis of the calixphyrin scaffold. Calixphyrins are considered as a special class of porphyrin analogue containing mixed sp<sup>2</sup>- and sp<sup>3</sup>-hybridized *meso*-carbon bridges.<sup>13</sup> The sp<sup>3</sup>-hybridized *meso*-carbon atoms disrupt the  $\pi$ -electron conjugation but provide intrinsic molecular flexibility to adopt a nonplanar (bent) conformation. The unique structure arising from the flexible scaffolds is advantageous to applications as molecular sensors,<sup>14</sup> anion-complexing agents,<sup>15</sup> and metal coordination ligands.<sup>16</sup> Sessler and co-workers have developed a general synthetic protocol of calixphyrin

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