



# Photophysical properties of organometallic complexes: Substituent effects



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## ABSTRACT

The literature data on the substituent influence on such properties,  $P$ , as the wavenumber maxima,  $\nu_{\text{abs}}$  and  $\nu_{\text{em}}$ , extinction coefficients,  $\epsilon$ , in the UV–Vis electronic spectra, as well as the quantum yields,  $\Phi_{\text{em}}$ , and emission lifetimes,  $\tau$ , for 31 series of organometallic complexes have been considered using correlation analysis. The  $P$  properties were first established to depend not only on the inductive and resonance effects but also on the polarizability of the substituent. The polarizability effect consists of an electrostatic attraction between the charge arising on the reaction centre owing to the change of electron distribution in the excited state and the dipole moments induced by this charge in the substituents. In specific cases, the polarizability effect has a dominant influence on the  $P$  properties. An understanding of the substituent effects may be useful for the design of devices based on the application of photophysical processes.

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## 1. Introduction

To date, there has been a considerable body of data on the photophysical properties,  $P$ , of organometallic complexes, see, for example, [1–39]. Such properties  $P$  as the wavenumber maxima,  $\nu_{\text{abs}}$ , and extinction coefficients,  $\epsilon$ , of the bands in the UV–Vis electronic absorption spectra, the wavenumber maxima,  $\nu_{\text{em}}$ , of the bands in the UV–visible emission spectra, the photoluminescence quantum yields,  $\Phi_{\text{em}}$ , and the emission lifetimes (i.e. the excited-state lifetimes),  $\tau$ , have been studied. These studies gave a clearer insight into the nature of excited states of organometallic complexes. It is remarkable that an investigation of the electronically excited states is important, not only from a theoretical standpoint. Interest in properties  $P(\nu_{\text{abs}}, \epsilon, \nu_{\text{em}}, \Phi_{\text{em}}, \tau)$  has recently quickened due to the fact that organometallic complexes are useful in many applications, such as the design of light-emitting diodes, light-emitting electrochemical cells, chemical sensors, magnetic devices etc. [8–39].

Judging from a large body of research [1–39], the properties  $P$  vary with the type of substituents. It is believed that a justified choice of substituents will allow the synthesis of organometallic complexes with the desired properties  $P$ , including those useful from a practical standpoint. However, this immediately raises an important question in regard to the mechanism of the interaction of the substituents with different reaction centres in electronically excited states of organometallic complexes. The problem is far from an exact solution at the present time. Thus so far, no consideration

has been given to the role of the polarizability effect. At the same time, it is well known that this effect is of considerable importance in organic and organometallic molecules bearing an excess charge on the reaction centre [40–55]. The aim of this paper is to elucidate the substituent effects influencing the photophysical properties  $P(\nu_{\text{abs}}, \epsilon, \nu_{\text{em}}, \Phi_{\text{em}}, \tau)$  of organometallic complexes such that contain the substituents X bound to an aromatic ring. We chose complexes of this type by virtue of the fact that they are now better understood and thus are well suited to attacking this problem.

## 2. Results and discussion

To our mind, a possible solution to the problem is to use correlation analysis of the so-called narrow series  $\text{XBR}_C$  which contain a reaction centre  $R_C$  and substituents X separated by a bridge group B. A distinctive feature of each concrete narrow series is that the fragment  $\text{BR}_C$  remains constant, whereas the substituents X vary. The narrow series I–XXXI of various complexes taken from the literature [1,2,4,5,9–11,14–16,19,21–24,26–38] are given in Tables 1–8.

First we considered three facets of the problem under discussion: classic and non-classic series; the peculiarities of the correlation analysis of the photophysical properties; the peculiarities of series I–XXXI.

### 2.1. Classic and non-classic series

For the purpose of the correlation analysis, it is convenient to separate narrow series into two categories: classic series and

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**Table 1**  
Photophysical data for series I–IV.

Series I		Series II		Series III		Series IV	
				[(p-XC <sub>6</sub> H <sub>4</sub> -C≡C) <sub>2</sub> Au <sub>2</sub> {PPh <sub>2</sub> N(Pr)PPh <sub>2</sub> }]		[(bpy) <sub>2</sub> Cd(μ-SC <sub>6</sub> H <sub>4</sub> X-p)] <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub> <sup>a</sup>	
X	ε(I) <sup>b</sup>	ν <sub>em</sub> (I) <sup>c</sup>	ε(II) <sup>d</sup>	ν <sub>em</sub> (III) <sup>e</sup>	ν <sub>abs</sub> (IV) <sup>f</sup>	ν <sub>em</sub> (IV) <sup>g</sup>	
H	17365	19100	4870	18850	28550	20150	
Me	16175	18500	–	20150	28250	18100	
tBu	21650	18800	–	–	–	–	
H <sub>2</sub> N	–	–	3410	–	–	–	
MeO	7105	18100	4190	20300	27600	17950	
Cl	–	–	4305	19900	28900	20400	

Wavenumber maxima  $\nu$  and extinction coefficients  $\epsilon$  are given in  $\text{cm}^{-1}$  and  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ , respectively.

<sup>a</sup> bpy = 2,2'-bipyridine.

<sup>b</sup> From Ref. [37], the metal-perturbed  $\pi$ - $\pi^*$  IL transition.

<sup>c</sup> From Ref. [37], the metal-perturbed  $^3[\pi$ - $\pi^*]$  IL state.

<sup>d</sup> From Ref. [19], the metal-perturbed  $\pi$ - $\pi^*$  IL transition.

<sup>e</sup> From Ref. [21], the triplet states of  $[\pi(\text{ArC}\equiv\text{C}) \rightarrow \pi^*(\text{PNP})]$  LLCT character.

<sup>f</sup> From Ref. [15], the LLCT transition.

<sup>g</sup> From Ref. [15], the LLCT emission.

**Table 2**  
Photophysical data for series V–VIII.

Series V		Series VI		Series VII		Series VIII	
[(bpy)Hg(μ-SC <sub>6</sub> H <sub>4</sub> X-p)] <sub>n</sub> (PF <sub>6</sub> ) <sub>n</sub>		p-XC <sub>6</sub> H <sub>4</sub> -CH = CHBmes <sub>2</sub> <sup>a</sup>					
X	ε(V) <sup>b</sup>	ν <sub>em</sub> (V) <sup>c</sup>	ν <sub>abs</sub> (VI) <sup>d</sup>	ν <sub>abs</sub> (VII) <sup>e</sup>	ν <sub>em</sub> (VII) <sup>f</sup>	ν <sub>abs</sub> (VIII) <sup>g</sup>	ν <sub>em</sub> (VIII) <sup>h</sup>
H	460	19150	30100	27100	22150	25900	19900
Me	640	18850	–	–	–	–	–
Bu	–	–	–	–	–	24900	19700
H <sub>2</sub> N	–	–	26900	–	–	–	–
Me <sub>2</sub> N	–	–	25250	25950	19450	19400	17650
MeO	510	18650	28750	26750	21550	22800	19100
MeS	–	–	28100	–	–	–	–
F	–	–	–	–	–	25650	19850
Cl	630	19000	–	27150	22300	–	–

Wavenumber maxima  $\nu$  and extinction coefficients  $\epsilon$  are given in  $\text{cm}^{-1}$  and  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ , respectively.

<sup>a</sup> mes = mesityl.

<sup>b</sup> From Ref. [16], the LLCT transition.

<sup>c</sup> From Ref. [16], the triplet states of a LLCT origin.

<sup>d</sup> From Ref. [22], the intramolecular charge-transfer (ICT) absorption.

<sup>e</sup> From Ref. [28].

<sup>f</sup> From Ref. [28], the excited states with ICT character.

<sup>g</sup> From Ref. [32], the  $\pi$ - $\pi^*$  transition.

<sup>h</sup> From Ref. [32], the excited states of  $^1(\pi\pi^*)$  character.

non-classic ones (refer e.g. [40–55]). The series of these categories differ essentially in substituent effects.

In classic series 4-XC<sub>6</sub>H<sub>4</sub>R<sub>C</sub><sup>q</sup>, bearing a positive or negative partial charge  $q$  on the reaction centre R<sub>C</sub>, the X substituents are located at a large distance  $d$  from R<sub>C</sub>, as the bridge B = C<sub>6</sub>H<sub>4</sub> is rather long. In these series the resonance interaction between the X substituent and the charged R<sub>C</sub><sup>q</sup> centre via the  $\pi$ -electron system (i.e. through resonance effect) is absent by definition. As is known [56], “a substituent attached to the benzene nucleus will affect to the electronic distribution within that nucleus.” The substituent

constants  $\sigma_p$  “... represent the measurement of this charge distribution by attachment of ...” the reaction centre R<sub>C</sub> “... to the p-position”. Thus the electronic influence of the X substituent can be expressed by its  $\sigma_p$  constant, involving inductive  $\sigma_I$  and resonance  $\sigma_R$  components. In the system of Hammett-Taft correlation equations, the chemical (logarithms of equilibrium and reaction rate constants) and physical properties  $P$  of the classic narrow series 4-XC<sub>6</sub>H<sub>4</sub>R<sub>C</sub><sup>q</sup> are described as follows:

$$P = P_H + a\sigma_p(\sigma_p^+, \sigma_p^-), \quad (1)$$

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