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Formation and Photoelectrochemical Properties of Charge Transfer Complexes between Fullerene and Metallophthalocyanine

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Abstract: The formation of charge transfer complexes (CTC) between C_{60} with metallophtha-locyanine (MPc, M=Zn, Co) has been investigated in three mixed organic solvents. The MPc-C_{60} CTC were characterized by using UV-Vis and fluorescence spectra. The formation equilibrium constants (*K*) of CTC and their stoichiometry were determined. The foundation of CTC leads to a remarkable enhancement of the photoelectrochemical property. The CTC will provide a potential opportunity to develop a new applicable photoelectric material.

Keywords: C_{60}, metalllophthalocyanine, photoelectrochemical property.

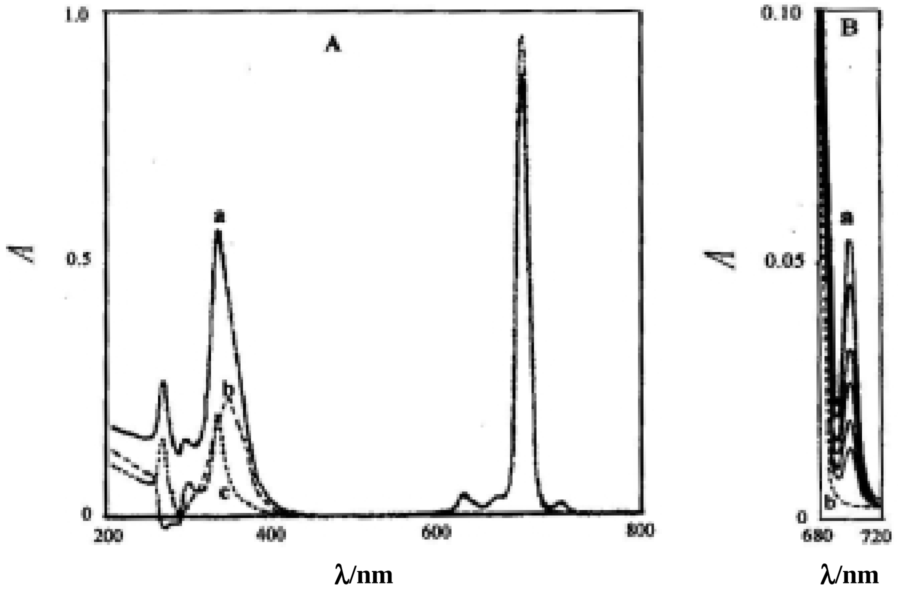
Fullerenes have generated a rapidly growing and active research area because of their unusual structure and physico-chemical properties. Fullerenes (C_{60} , C_{70}) have higher electron affinity (2.75ev), so it is well known that they are excellent electron acceptors and have a large number of conjugated π bonds which may lead to large non-linear polarizabilities[1]. C_{60} is reported to form charge transfer complexes (CTC) with appropriate electron donors, for example, polymolecular PVK, γ-cyclodextrin, aromatic and aliphatic amines[1-3]. The charge-transfer interaction greatly enhances the second-order optical non-linearity of organic molecules, so C_{60}-based CTC shall be an interesting material with non-linear optical properties. Metallophthalocyanines (MPc) have a large π conjugated system too. They are rich in electrons as an organic semiconductor and may be used as a good photovoltaic material in solar cell, but CTC of C_{60} with MPc has never been reported. Here we report the formation of CTC between C_{60} and MPc and the photovoltaic effect of MPc-C_{60} CTC with various systems.

The formation and characterization of MPc-C_{60} CTC

We chose three mixed organic solvents with different polarities as research system (**Table 1**) in which C_{60} and MPc can be dissolved. After reaction for 12-36 h at 48-80 ℃ the color of the reaction system became lighter gradually. CTC of C_{60} with MPc can be characterized by the change in UV-Vis absorption, fluorescence and laser Raman spectra.

The UV-Vis absorption shows a new peak of charge transfer band at 710 nm (**Figure 1**) for formation of ZnPc-C_{60} CTC. In the 260-420 nm region, the absorption

Figure 1. A. UV-Vis spectra of ZnPc-C_{60} (a), ZnPc (b) and C_{60} (c) in S1 solvent system   B. UV-Vis spectra of ZnPc-C_{60} (a), ZnPc (b)



band is similar to that of C_{60}, but there is also an increase in the absorption strength and broad-band for CTC. The molar concentrations of C_{60}, ZnPc, ZnPc-C_{60} are the same (5×10^{-5} mol/L) but optical densities of C_{60}, ZnPc, CTC are 0.20, 0.24, 0.58, respectively at 333 nm. The increase in the absorption strength can be attributed to the lowering of symmetry due to the formation of CTC[1]. Similar observation has been made for CoPc-C_{60} CTC which shows a new peak at 700 nm. Additional evidence for the formation of MPc-C_{60} comes from the fluorescence quenching of ZnPc by C_{60}. It shows that the fluorescence of ZnPc is regularly quenched with the progressive addition of C_{60} and the largest quenching appears when the molar ratio of ZnPc to C_{60} is 1:1. Assuming an equilibrium to be present, the formation equilibrium constant (K) of ZnPc-C_{60} CTC can be determined by employing the Benesi-Hilderbrand equation[4]:

$$\mathrm{nMPc} + C_{60} \rightarrow (\mathrm{MPc})_n\text{-}C_{60}$$

$$\frac{[C_{60}]\cdot l}{\mathrm{A}} = \frac{1}{K\cdot\varepsilon\cdot[\mathrm{MPc}]^n} + \frac{1}{\varepsilon}$$

Here A is the absorbance of MPc-C_{60} CTC at 330 nm, ε is extinction coefficient. A plot of $[C_{60}]$/A *vs.* 1/[MPc] gave a straight line (R=0.9953) from which ε and equilibrium constant K have been determined (**Table 1**). Although **Table 1** shows existence of a 1:1 CTC, but it can be transformed to 2:1 CTC at higher temperature in the solvent system of toluene with DMSO.

Table 1. Molar extinction coefficient (ε) and equilibrium constant (K) of ZnPc-C_{60}

Solvent system	Reaction temperature	Composition of ZnPc- C_{60}	ε ($mol^{-1}\cdot L\cdot cm^{-1}$)	K ($mol^{-1}\cdot L$)
S1:TOL+$C_2H_2Cl_4$	40℃	1:1	7.83×10^4	1.73
S2:TOL+THF	40℃	1:1	1.24×10^4	1.13
S3:TOL+DMSO	40℃	1:1	8.08×10^4	1.05
	80℃	2:1	7.70×10^4	1.02 ($mol^{-2}L^2$)

The photovoltaic effect of MPc-C_{60} CTC thin film on semiconductor electrodes

Metallophthalocyanines have attracted attention as organic semiconductors and may be used as good photovoltaic transfer materials in solar cell because they are stable, and have higher absorption in the visible region and relatively better photovoltaic properties. Their photoelectrochemical behavior of MPc films on semiconductor electrodes GaAs have been demonstrated by photoelectrochemical cells. While CTC of C_{60} with MPc has been formed there is a great influence of C_{60} on photovoltaic effect (PVE) of MPc.

The PVE has been studied by the photoelectrochemical cell[5]. The working electrode is single crystal GaAs covered with a homogeneous thin film (1 μm) of MPc-C_{60}. The cell, painted black, is equipped with an optical window to allow irradiation of the electrode. The light source is 500 w Xe lamp and to give a light flux of 500 mW/cm^2 on the surface of electrode. A saturated calomel electrode (SCE) serves as the reference and a Pt foil as the counter electrode. The redox couples of media are I_3^-/I^-, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, O_2/H_2O (in KCl solution). Under the dark and illuminated states the photogenerated voltage (ΔV) and currency (ΔI) are measured in the redox couples of media (**Table 2**).

Table 2. The PVE of MPc-C_{60}/GaAs in various media, **ΔV** (mV) and **ΔI** (μA)

Electrode	I_3^-/I^-		$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$		O_2/H_2O (KCl)	
	ΔV	ΔI	ΔV	ΔI	ΔV	ΔI
ZnPc/GaAs	151.8	11.9	308.4	19.6	258.6	45.7
ZnPc-C_{60}/GaAs	575.3	413.0	409.5	18.7	451.0	54.7
CoPc/GaAs	192.0	25.0	180.0	18.5	150.0	43.0
CoPc-C_{60}/GaAs	525.0	276.0	548.0	223.0	376.0	70.8

The results show that the formation of MPc-C_{60} CTC leads to a remarkable enhancement of the photoelectrochemical property. The MPc-C_{60} and GaAs form heterojunction photoelectrode that can increase the photo-absorption efficiency in the UV-Vis region. There is a better overlap of the π orbital between MPc-C_{60}, and photoexcited CTC improves the photogeneration and conduction of charge carriers. The ΔV and ΔI values of the CTC are 2-3 times more than those of MPc. So the charge-transfer complexes of MPc-C_{60} will provide a potential opportunity to develop a new applicable photoelectric material.

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