



# Photoinduced electron-transfer from benzimidazole to nanocrystals

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## ABSTRACT

The dynamics of photoinduced electron injection and energy transfer from benzimidazole to CuO, Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles has been studied by FT-IR, absorption and fluorescence spectroscopic methods. The association between nanoparticles and the benzimidazole derivative was explained from both absorption and fluorescence quenching data [ $K_{app} = 2.11 \times 10^6 \text{ M}^{-1}$  (CuO);  $4.11 \times 10^6 \text{ M}^{-1}$  (Fe<sub>2</sub>O<sub>3</sub>);  $2.91 \times 10^6 \text{ M}^{-1}$  (WO<sub>3</sub>) and  $3.85 \times 10^6 \text{ M}^{-1}$  (Al<sub>2</sub>O<sub>3</sub>)]. There is good agreement between these values of  $K_{app}$  obtained from the data of fluorescence quenching with those determined from the absorption spectral changes which highlighted the validity of the association between benzimidazole and nanoparticles. The distance between the benzimidazole derivative and nanoparticles ( $r_0 \sim 3.12 \text{ nm}$ ) as well as the critical energy transfer distance ( $R_0 \sim 1.70 \text{ nm}$ ) has been calculated. By applying the Rehm–Weller equation, the free energy change ( $\Delta G_{et}$ ) for electron injection has also been calculated.

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## 1. Introduction

Nanotechnology, inextricably a multidisciplinary field, has an explosive growth in the past decade due to its extremely hefty applications in various fields of nanoscale electronics, optics, magnetics, energy, catalysis, nano medicines, clothing, cosmetics, etc. [1]. Nanocrystalline semiconductors with unique properties such as large surface area, pore structure, embedded effect and size effect are recognized to have potential applications in genomics, proteomics and bioanalytical fields. The combination of nanoparticles and biological molecules has attracted tremendous attention, where nanoparticles could present a versatile nanoscale interface for biomolecular recognition [2–4]. Some researchers have reported the specific interaction between nanoparticles and protein as well as other biomolecules [5–9]. The electron-transfer process at the semiconductor–dye interface has been successfully utilized in the development of solar cells, electronic devices, heterogeneous photocatalysis and waste water treatment [10,11]. The efficiency of these processes depends on the properties of the sensitizers, semiconductor and their interaction under photo excitation. Recently, semiconductor composite nanostructures have become an attractive topic because of their potential applications in different fields [12].

Imidazoles display a broad spectrum of biological activities such as antiviral, antiulcer, antihypertension and anticancer properties [13]. They have also found application as a chromophore with high extinction coefficient, readily tunable absorption wavelength, and fluorophoric properties and are desirable as a large planar synthetic building block

in supramolecular chemistry [14]. They are important building blocks for the synthesis of proton, anion and cation sensors. As far as our knowledge is concerned, detailed study on the photoinduced interaction of nanoparticles with bioactive benzimidazole derivatives [15] has not been reported till now. The fluorescence quenching technique is applied to study the interaction between nanomaterials and the benzimidazole derivative to infer the association and also the energy transfer between them (Scheme 1). According to the plot of  $\log [(F_0 - F)/F]$  versus  $\log [\text{nanoparticles}]$ , the binding constants have been determined. Further, the mechanism of electron transfer process on the basis of energy level diagram has also been proposed in this paper. Distances between the benzimidazole derivative and nanosurfaces ( $r_0 \sim 3.12 \text{ nm}$ ) as well as the critical energy transfer distance ( $R_0 \sim 2.30 \text{ nm}$ ) have also been calculated.

## 2. Materials and methods

### 2.1. Materials

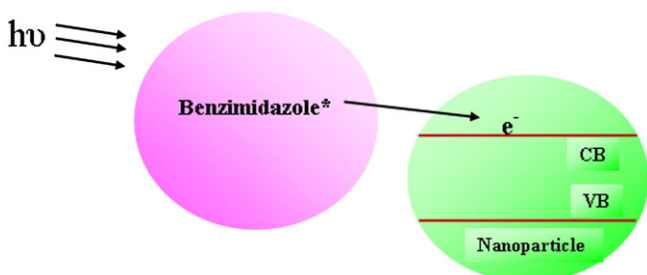
Benzaldehyde, o-phenylenediamine and all other reagents have been purchased from Himedia chemicals and used without further purification. The nanoparticles used were those supplied by Sigma-Aldrich and characterized by Karunakaran et al. [16]; the average crystal size (D) and surface area (S) are listed in Table 1.

### 2.2. Measurements

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the ligand have been recorded on a Bruker 400 MHz NMR instrument. Mass spectrum was recorded using Agilent 1100 mass spectrometer. The fluorescence quenching measurements have been carried out using a Perkin Elmer LS55

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Scheme 1. Photoinduced charge injection and charge separation.

spectrofluorometer. The excitation wavelength was 271 nm and the emission was monitored at 361 nm. The excitation and emission slit widths (each 5 nm) and scan rate ( $600 \text{ nm min}^{-1}$ ) were kept constant for all the measurements. The absorption spectral measurements were recorded by using a Perkin Elmer Lambda 35 spectrophotometer. An ethanolic solution of the benzimidazole derivative of required concentration ( $1 \times 10^{-8} \text{ M}$ ) was mixed with nanoparticles dispersed in ethanol at different loadings and the absorbance and emission spectra were recorded.

### 2.3. General procedure for the synthesis of ligand

A mixture of benzaldehyde (2 mmol), *o*-phenylenediamine (1 mmol) and ammonium acetate (2.5 mmol) was refluxed at  $80^\circ \text{C}$  in ethanol. The reaction was monitored by TLC and purified by column chromatography using petroleum ether:ethyl acetate (9:1) as the eluent.

#### 2.3.1. 1-benzyl-2-phenyl-1H-benzo[d]imidazole

Yield: 50%. mp =  $124^\circ \text{C}$ , anal. calcd. for  $\text{C}_{20}\text{H}_{16}\text{N}_2$ : C, 84.48; H, 5.67; N, 9.85. Found: C, 84.12; H, 5.79; N, 10.09.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.43 (s, 2H), 7.125–7.140 (d, 2H) ( $J = 6 \text{ Hz}$ ), 7.23–7.28 (m, 2H), 7.32–7.37 (m, 4H), 7.45–7.50 (m, 3H), 7.71–7.72 (t, 2H) ( $J = 5.4 \text{ Hz}$ ), 7.90–7.91 (d, 1H) ( $J = 6.8 \text{ Hz}$ ).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  48.39 (– $\text{CH}_2$  carbon), 110.53, 120.02, 122.68, 123.04, 125.99, 127.78, 128.76, 129.06, 129.28, 129.91, 130.14, 136.10, 136.43, 143.24, 154.19 (aromatic carbons). MS:  $m/e$  284.3, calcd. 285.13 [ $\text{M} + 1$ ].

## 3. Results and discussion

### 3.1. Absorption of benzimidazole derivative-nanoparticles

The absorption spectra of the benzimidazole derivative in the presence of  $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{WO}_3$  and  $\text{Al}_2\text{O}_3$  nanoparticles dispersed at different loadings and also in their absence are displayed in Fig. 1 and the values are tabulated in Table 2. The nanoparticles enhance the absorbance of the benzimidazole derivative remarkably without shifting its absorption maximum (361 nm). This indicates that the nanocrystals do not modify the excitation process of the ligand. The enhanced absorption at 271 nm observed with the dispersed semiconductor nanoparticles are due to adsorption of the benzimidazole derivative on the semiconductor surface. This is because of effective transfer of electron from the excited state of the benzimidazole derivative to the conduction band of the semiconductor nanoparticles. However, this inference is not

applicable to alumina; alumina is an insulator and the possible explanation is energy transfer from the excited state of the ligand to the alumina lattice.

### 3.2. FT-IR characteristics of benzimidazole derivative-nanoparticles

Fig. 2 shows the FT-IR spectra of the benzimidazole derivative (broken line) and it is bound to the nanoparticle (solid line). The spectrum of the benzimidazole derivative shows the  $>\text{C}=\text{N}$  stretching vibration at  $1604 \text{ cm}^{-1}$ . This band is shifted in the benzimidazole derivative bound to nanoparticle; a new band appears at  $1633 \text{ cm}^{-1}$ . These observations show that the benzimidazole derivative is adsorbed on the surface of nanoparticles.

### 3.3. Fluorescence quenching characteristics

Addition of nanoparticles to the solution of the benzimidazole derivative resulted in the quenching of its fluorescence emission and the values are tabulated in Table 3. Fig. 3 displays the effect of increasing concentration of nanoparticles on the fluorescence emission spectrum of benzimidazole derivative [17]. The apparent association constants ( $K_{\text{app}}$ ) have been obtained from the fluorescence quenching data using the following equation

$$1/(F_0 - F) = 1/(F_0 - F) + 1/K_{\text{app}}(F_0 - F)[\text{nanoparticles}] \quad (1)$$

where  $K_{\text{app}}$  is the apparent association constant,  $F_0$  is the initial fluorescence intensity of the benzimidazole derivative,  $F$  is the fluorescence intensity of the benzimidazole derivative adsorbed on nanoparticles and  $F$  is the observed fluorescence intensity at its maximum. A good linear relationship between  $1/(F_0 - F)$  and the reciprocal concentration of nanoparticles is seen. From the slope, the values of apparent association constants ( $K_{\text{app}}$ ) have been assessed for benzimidazole derivative-nanoparticles.

The fluorescence quenching behavior is usually described by the Stern–Volmer relation:

$$I_0/I = 1 + K_{\text{SV}} [Q] \quad (2)$$

where,  $I_0$  and  $I$  are the fluorescence intensities in the absence and presence of quencher,  $K_{\text{SV}}$  is the Stern–Volmer constant related to the bimolecular quenching rate constant and  $Q$  is the quencher (Fig. 4).

The ability of the excited state benzimidazole derivative to inject its electrons into the conduction band of nanoparticles is determined from the energy difference between the conduction band of nanoparticles and excited state oxidation potential of the benzimidazole derivative. According to the equation  $E_{s^*/s^+} = E_{s/s^+} - E_s$ , the oxidation potential of excited singlet state benzimidazole derivative is  $-1.97 \text{ V}$  (vs. NHE), where,  $E_{s/s^+}$  is the oxidation potential of the benzimidazole derivative,  $0.21 \text{ V}$  (vs. NHE) and  $E_s$  is the excited state energy,  $2.18 \text{ eV}$ ; the excited state energy of the benzimidazole derivative is calculated from the fluorescence maximum based on the reported method [18]. The energy level of the conduction band of semiconductor nanoparticles is shown in Scheme 2 [19]. It suggests that the electron transfer from excited state benzimidazole derivative to the conduction band of nanoparticulate semiconductors is energetically favorable.

### 3.4. Binding constant and number of binding sites

Static quenching arises from the formation of complex between fluorophore and the quencher and the binding constants ( $K$ ) have been calculated by using the equation

$$\log[(F_0 - F)/F] = \log K + n \log [Q] \quad (3)$$

where  $K$  is the binding constant of nanoparticles with benzimidazole derivative and the calculated binding constant values are  $[2.11 \times 10^6 (\text{CuO})$ ,

Table 1  
Crystallite size (D), surface area (S) and apparent association constants ( $K_{\text{app}}$ ).

Nanocrystal	Crystal structure	D (nm)	S ( $\text{m}^2 \text{g}^{-1}$ )	$10^{-6} K_{\text{app}}$
$\delta, \gamma\text{-Al}_2\text{O}_3$	Cubic:tetragonal :: 0.65:0.35	11	148	3.85
$\text{WO}_3$	Primitive monoclinic	23	39	2.91
$\delta\text{-Fe}_2\text{O}_3$	Cubic	28	33	4.11
$\text{CuO}$	End centered monoclinic	32	36	2.11

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