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Ground and excited state intramolecular proton transfer controlled intramolecular charge separation and recombination: A new type of charge and proton transfer reaction

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ABSTRACT

A novel β-diketone 1-(4-(9-carbazol)phenyl)-3-phenyl-1,3-propanedione (CDBM) has been synthesized. When excited at 380 nm, this molecule shows single fluorescence. However, when excited at 338 nm, it shows dual fluorescence. A Al^{3+} complex $Al(CDBM)_3$ has been synthesized to investigate the dual fluorescence of CDBM. It is found that this complex shows single fluorescence under all excitation. This result indicated that the dual fluorescence of CDBM may relate to the intramolecular proton transfer reaction. Based on the experimental and theoretical studies of CDBM, *N*-(4-cyanophenyl)carbazole (CBN) and $Al(CDBM)_3$, a "ground and excited state intramolecular proton transfer controlled intramolecular charge separation and recombination" mechanism is proposed to explain the unusual excitation-dependent dual fluorescence of CDBM.

1. Introduction

Charge and proton transfer reactions are both fundamental chemical processes occurring in nature. Intensive studies can be found in the literature for both subjects [1–6]. It is particularly interesting when both processes are feasible in one molecule. One prototype of such systems is 4′-(diethylamino)-3-hydroxyflavone [7,8]. This molecule exists in its energetically favorable normal form (N) in ground state. After excitation, it is promoted to the intramolecular charge transfer (ICT) excited state N^*. At the same time, N^* can be transformed into a tautomer form (T^*) through excited state intramolecular proton transfer (ESIPT) reaction. Dual fluorescence can be observed when the two forms decay to their corresponding ground states [7,8]. New cases have been reported such as HBOCE and HBODC, which show strong solvatochromic fluorescence from ESIPT/ICT process [4]. However, the dual fluorescence of these molecules is excitation-independent and the charge transfer (CT) is controlled by the intramolecular proton transfer only in the excited states.

In this paper, we report for the first time an interesting excitation-dependent dual fluorescence phenomenon of a donor–acceptor–acceptor type β-diketone 1-(4-(9-carbazol)phenyl)-3-phenyl-1,3-propanedione (CDBM). This molecule shows single fluorescence (Band A), dual fluorescence (Bands A and B) as the excitation wavelength varies from 380 nm (around the first absorption band) to 338 nm (around the second absorption band). Both fluorescence bands show great solvatochromic shifts with increasing solvent polarity. In order to study the relationship between the dual fluorescence and the intramolecular hydrogen bonding of CDBM, the complex $Al(CDBM)_3$ has been synthesized by coordinating CDBM to Al^{3+} ion. The photophysical properties (lifetimes and bathochromic shifts) of the model compound *N*-(4-cyanophenyl)carbazole (CBN), CDBM and $Al(CDBM)_3$ have been studied systematically. The excited state dipole moments of the three compounds were determined with fluorescence solvatochromic method. Ground state geometries and energies of these compounds were calculated by density functional theory. Finally, the mechanism of the unusual excitation-dependent dual fluorescence of CDBM was discussed based on the experimental and theoretical investigations.

2. Experimental and computational details

2.1. Experimental details

N-(4-cyanophenyl)carbazole (CBN) was synthesized from 4-fluorobenzonitrile and carbazole by a simple procedure according to the literature [9]. The crude product was purified by

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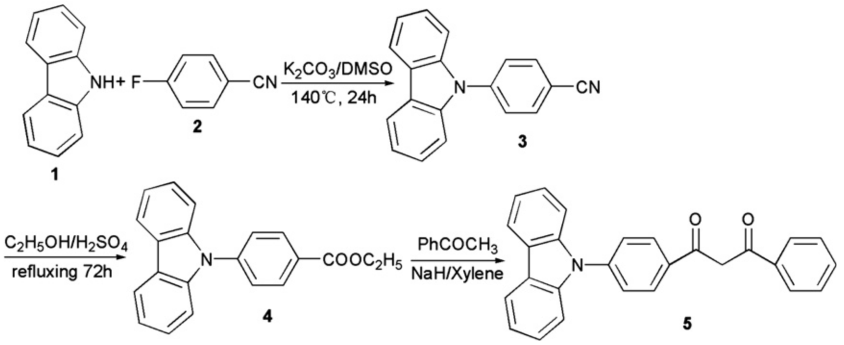


Scheme 1. Synthetic procedure of CDBM.

recrystallization and subsequent column chromatography. CDBM was synthesized as follows (Scheme 1): 2.7 g (10 mmol) CBN, 15 ml H_2SO_4 and 50 ml C_2H_5OH were added to a 100 ml round-bottomed flask and heated to reflux for 3 days. The mixture was poured into 500 ml water and then extracted with CH_2Cl_2. The product ethyl 4-(9-carbazol)benzoate (**4** in Scheme 1) was purified by column chromatography with CH_2Cl_2–petroleum ether (1:2, v/v) as eluent to give 2.41 g (76%) of **4**. To a three-neck flask (100 ml), sodium hydride (0.28 g, 70%, 16 mmol) washed with anhydrous hexane and anhydrous ether (60 ml), 2.41 g (8 mmol) **4** and 1.92 g (16 mmol) acetophenone were added sequentially. The mixture was stirred for 48 h under N_2 at room temperature and acidified by hydrochloric acid to pH 2–3, then the solvent was vaporized and the solid was purified by silica column chromatography with CH_2Cl_2–petroleum ether (1:1, v/v) as eluent to give CDBM with yield of 42%. ^{1}H NMR (CD_3CN, TMS): δ (ppm) 7.16 (s, 1H), 7.33 (t, 2H, J = 7.40, 7.04 Hz), 7.46 (t, 2H, J = 8.17, 7.21 Hz), 7.51–7.59 (m, 4H), 7.65 (t, 1H, J = 7.26, 7.27 Hz), 7.79 (d, 2H, J = 8.37 Hz), 8.12 (d, 2H, J = 7.36 Hz), 8.20 (d, 2H, J = 7.76 Hz), 8.33 (d, 2H, J = 8.43 Hz), 17.14 (s, 1H). Anal. Calc. for $C_{27}H_{19}NO_2$: C, 83.27; H, 4.92; N, 3.60. Found: C, 83.08; H, 4.93; N, 3.44.

The complex Al(CDBM)$_3$ was synthesized according to the following procedure: To a 50 ml round-bottomed flask, CDBM (1.167 g, 3.0 mmol), NaOH (0.120 g, 3.0 mmol) were mixed in 10 ml ethanol and refluxed for 10 min, then it was added dropwise to 10 ml ethanol solution of $AlCl_3$ (0.146 g, 1.1 mmol). The mixture was refluxed for 2 h and then poured into water. The crude product was obtained by filtration and purified by recrystallization in a mixture of THF–ethanol. ^{1}H NMR ($CDCl_3$, TMS): δ (ppm) 7.11 (t, 3H, J = 8.03, 7.56 Hz), 7.29 (d, 6H, J = 7.50 Hz), 7.38–7.49 (m, 21H), 7.63–7.67 (m, 6H), 8.13 (t, 12H, J = 8.12, 7.14 Hz), 8.31–8.34 (m, 6H). Anal. Calc. for $C_{81}H_{54}AlN_3O_6$: C, 81.60; H, 4.57; N, 3.52. Found: C, 80.95; H, 4.72; N, 3.82.

All spectroscopic grade solvents were purchased from ACROS.

Absorption spectra were recorded with Shimadzu UV 3100 spectrophotometer, and steady state fluorescence spectra were taken with an Edinburgh Instruments FLS920 spectrometer. All the fluorescence spectra were corrected for the instrument response using a correction file provided by the manufactory. Fluorescence quantum yields were determined using quinine sulfate in 1.0 N H_2SO_4 as a standard (Φ_f = 0.546 at 25 °C) [10,11].

Lifetimes longer than 1 ns were measured with Edinburgh Instruments FLS920 based on the time correlated single photon counting technology. A hydrogen filled nanosecond flash lamp was used as the excitation source and the signals were detected with a photomultiplier (Hamamatsu R955). A picosecond lifetime spectrometer Edinburgh Instruments Lifespec-Red was used to measure lifetimes shorter than 1 ns. In this equipment, a diode laser (operating at 372 nm, pulse duration 69 ps) controlled by a picosecond light pulser (Hamamatsu PLP-10) was used as excitation source. By processing the lifetime data with the F900 reconvolution software, a time resolution better than 1 ns for FLS920 and 20 ps for Lifespec-Red can be achieved.

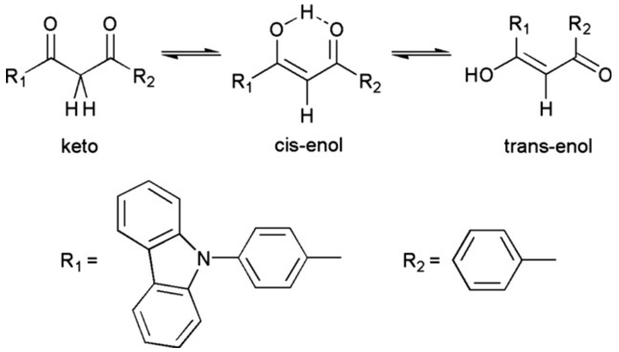
2.2. Computational details

The quantum chemical calculations were performed using the GAUSSIAN 03 package [12]. Ground state geometries of CBN, CDBM and Al(CDBM)$_3$ have been optimized with the B3LYP [13] functional and a 6-31G(d) [14] basis set with no symmetry constraints. Numerical frequency calculations were performed with the same functional and basis set to determine the nature of the stationary point. The ground state dipole moments were calculated using the semi-empirical AM1 [15,16] method.

3. Results and discussion

3.1. Keto/enol equilibrium in solution

In general, β-diketones exist in three tautomeric forms in solution: keto, *cis*-enol and *trans*-enol form [17–19]. Scheme 2 illustrates the keto-enol equilibrium of CDBM. Because R_1 and R_2 are different, there are more than one *cis*-enol form and *trans*-enol form of CDBM. Scheme 2 only shows one of them for clarity. Among these tautomers, *cis*-enol forms are considered to be the photochemical stable ones because they are stabilized by the intramolecular hydrogen bonding and the conjugated system [17,20]. Theoretical studies have shown that the energies of *trans*-enol form β-diketones are much higher than their *cis*-enol isomers [20,21]. Therefore, they can only be observed experimentally at very low temperatures [21,22]. Because our experiments were all carried out at room temperature, it is reasonable to only consider the existence of keto and *cis*-enol forms. ^{1}H NMR spectrum of ca. 10^{-3} mol l^{-1} CDBM in



Scheme 2. Keto-enol equilibrium of CDBM.