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β-Diketones bearing electron-donating chromophores and a novel β-triketone: synthesis and reversible fluorescence behavior

Xin Zhang, Zi-Chen Li,* Ning Xu, Kai-Bo Li, Song Lin, Feng-Zhu Lu, Fu-Sheng Du and Fu-Mian Li

Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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Abstract—Saturated and unsaturated β-diketones bearing 4-*N*,*N*-dimethylaminophenyl substituent and a novel β-triketone were synthesized. These β-diketones exist in both *cis*-enol and keto forms in solution, and their relative contents were determined by ^{1}H NMR measurements. In contrast, for the β-triketone, only enol form was observed in a solution. A strong fluorescence quenching was observed for unsaturated diketones as compared with the saturated ones. These β-diketones displayed reversible photoinduced ketonization as revealed by UV–vis spectroscopy. The fluorescence emission of the saturated β-diketones faded gradually during UV irradiation. The fluorescence emission of these saturated β-diketones can thus be reversibly switched between the enol form 'ON' and the keto form 'OFF' based on keto-enol tautomerization.

β-Diketones are well known to have two forms, that is enol and keto forms. One of the most interesting properties is the conversion between the two forms, which was termed as keto-enol tautomerism.[1] The enol form is more stable than the keto form in a solution, and the tautomeric equilibrium can be affected by various factors such as solvent polarity,[2] substitution groups,[3] pH values, and UV light irradiation.[4] The photoinduced ketonizations of β-diketones generally occur after UV irradiation.[5] The photoinduced ketonization process is reversible. In the darkness the keto form can be converted to the *cis*-enol form.[6,17] Although a wide range of β-diketones and their keto-enol tautomerism have been studied extensively, little attention was paid to their fluorescence behavior because of the general fluorescence quenching of the n–π* triplet states of β-diketones.

For the past decade, we had studied the synthesis, polymerization, and fluorescence behavior of vinyl and maleimide monomers bearing electron-donating or electron-accepting chromophores.[7,8] Here, we designed and synthesized new β-diketones **1** and **2**, which contain electron-donating chromophores as shown in Scheme 1. The corresponding unsaturated β-diketone **3** was also synthesized, which was symbolized as $A_{(=)}$–D,[8] where $A_{(=)}$ is the electron-accepting C=C bond attached with β-diketone groups, and D is the *N*,*N*-dimethylaniline donor. In addition, as an extension of β-diketones, a novel β-triketone **4** was synthesized. Their keto-enol tautomerism and fluorescence behaviors were investigated. To the best of our knowledge, this is the first report on the reversible fluorescence behavior based on keto-enol tautomerism.

For the synthesis of β-diketones, several synthetic routes have been developed: (1) Claisen condensation of corresponding esters with esters, or ketones with esters in the presence of sodium hydride (NaH), tetramethyl orthosilicate/cesium fluoride, sodium ethoxide, or *n*-butyllithium;[9–11] (2) acylations of β-alkylketones with acid chlorides in the presence of pyridine or triethylamine;[12] and (3) aldol condensation of aldehydes or β-alkylketones to yield the 3-hydroxyl ketones, followed by an oxidation.[13] β-Diketones **1** and **2** were synthesized using the route (1) by Claisen condensation of 1-(4-(dimethylamino)phenyl) ethanone with ethyl acetate and methyl pivalate, respectively, using dibenzo-18-crown-6 and ethyl ether/diethylene glycol dimethyl ether (5/1, v/v) as solvents in the presence of sodium hydride (NaH) as shown in Scheme 1. The synthesis of β-diketones **3**

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[*] Corresponding author. Tel.: +86 10 6275 1708; fax: +86 10 6275 7155; e-mail: zcli@pku.edu.cn

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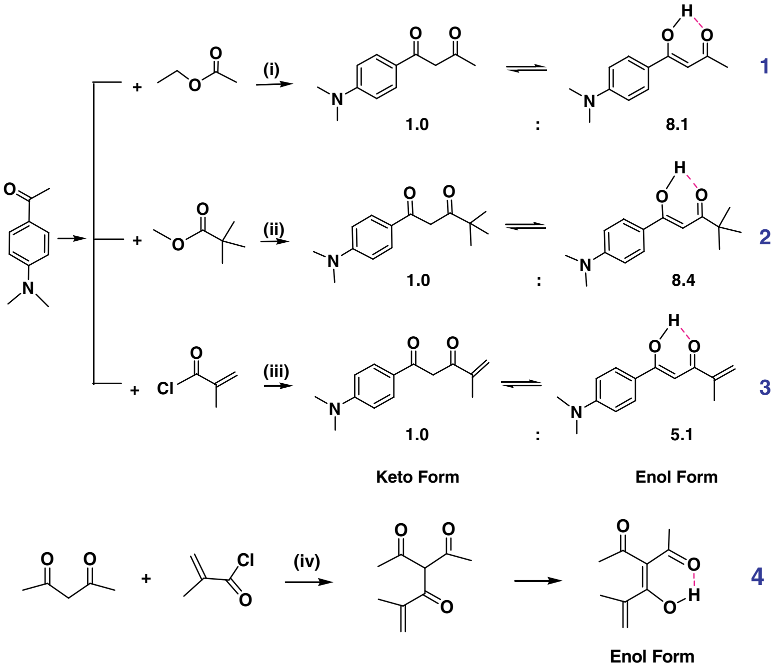


Scheme 1. Synthetic routes to the saturated β-diketones **1** and **2**, the unsaturated β-diketone **3**, and β-triketone **4**. Reagents and conditions: (i) NaH, dibenzo-18-crown-6, rt; (ii) NaH, Et_2O/diglyme (5/1, v/v), rt; (iii) $NaNH_2$, Et_2O/diglyme (4/1, v/v); (iv) Mg $(OC_2H_5)_2$, Et_2O/EtOH (4/1, v/v), 0–5 °C.

and **4** is based on an improved acylation employing diethyl ether/diethylene glycol dimethyl ether (4/1, v/v) as solvent under strong basic conditions, that is sodium amide ($NaNH_2$) for **3** and magnesium ethanolate ($Mg(OC_2H_5)_2$) for **4**. There are few reports on the acylation reaction under such strong basic conditions. The synthetic details and spectroscopic characterizations were provided in Supplementary materials.

Four compounds were characterized with H NMR spectroscopy. The singlets at δ 4.00 of **1**, δ 4.04 of **2**, δ 4.23 of **3** were assigned to the methylene protons ($–CO–CH_2–CO–$) of the corresponding keto tautomers. The singlets at δ 6.08 of **1**, δ 6.17 of **2**, δ 6.34 of **3** were assigned to the vinyl protons ($–C(–OH){=}CH–$) of the corresponding enol tautomers. The singlet at δ 16.45 of **1**, δ 16.82 of **2**, δ 16.40 of **3**, δ 16.64 of **4** were assigned to the hydroxyl protons (OH) of the corresponding enol tautomers. The chemical shifts of the enolic hydroxyl protons became sharp and shifted downfield as compared with the hydroxyl protons in general, suggesting the existence of strong H-bonding. These results indicate that the β-diketones **1**, **2**, and **3** exist in two forms, that is keto and enol forms in a solution.

According to the assignments of ^1H NMR peaks, the relative ratios of enol versus keto tautomers are 8.1/1.0 for **1**, 8.4/1.0 for **2**, 5.1/1.0 for **3** in $CDCl_3$, which were calculated from the integral ratios of the enolic vinyl and ketonic methylene (1/2) protons. The enol form predominates. The enol/keto ratios of the β-diketones **1**, **2**, and **3** in acetonitrile-d_3 are 3.9/1.0, 4.1/1.0, and 3.2/1.0, respectively. This may be due to the fact that intramolecular H-bonding interaction was weakened in acetonitrile therefore the less contents of the enol forms.

For β-triketone **4**, the NMR signal of the ketonic methenyl proton ($CH(COR)_3$) was not observed. The integral ratio (9.05/1.00) of the resonance peaks of the methyl protons ($2(CH_3CO)–$ and $CH_3C(R){=}$) and enolic hydroxyl proton (OH) indicates that the β-triketone **4** only exists in one form, that is enol form in a solution as illustrated in Scheme 1.

These β-diketones are thermally unstable as revealed by thermal gravimetric analysis (TGA)/differential thermal analysis (DTA) measurements (Figs. S-4 and S-5, and Scheme S-1 in Supplementary materials).

Compared with the saturated β-diketones **1** and **2**, the absorption spectra of unsaturated $A_{(=)}$–D **3** show a bathochromic shift of 22 nm as shown in Figure 1. This

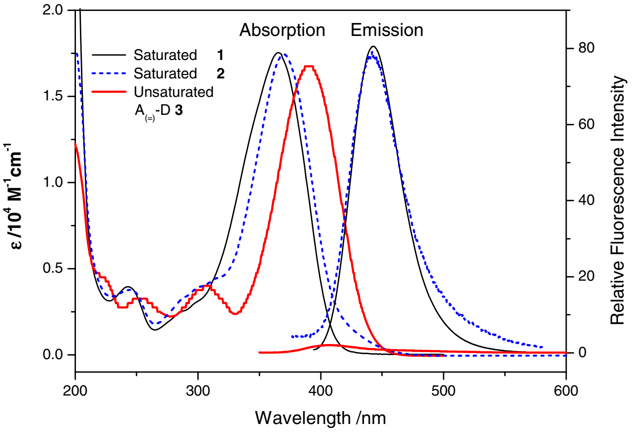


Figure 1. UV–vis absorption and fluorescence spectra of the saturated β-diketones **1** and **2**, the unsaturated β-diketone **3** in acetonitrile. Concentration: 2.0×10^{-5} M.

may be attributed to the more extended and conjugated structure of the enol form of unsaturated **3**. In contrast, their fluorescence spectra are distinct. The saturated β-diketones **1** and **2** display a strong fluorescence in acetonitrile with the quantum yields (Q)[14] of 2.41% and 2.35%, respectively. However, very weak fluorescence ($Q < 0.02\%$) was observed for the unsaturated $A_{(=)}$–D **3** as shown in Figure 1.

For β-diketone **1,** the absorption intensity at the long wavelength of 365 nm (π–π* transition of the enol structure)[15,16] was decreased gradually during UV irradiation as shown in Figure 2. A new absorption peak at the short wavelength of 337 nm (attributed to the keto structure)[16] appeared and increased gradually. An isosbestic point was observed at 348 nm, implying that the keto tautomer increased and the enol tautomer decreased during UV irradiation. This process is called as photoinduced ketonization or photoketonization.[1] The photoinduced ketonization was also observed for **2** and **3**.

Interestingly, the fluorescence emission of β-diketone **1** was found to be fading during UV irradiation, as shown in Figure 3A. The fluorescence quantum yields dramatically decrease from 2.41% before UV irradiation to a very low value (<0.05%) after UV irradiation. The fluorescence behavior can be rationalized by the enol-keto tautomerism. In the *cis*-enol form, the hydroxyl and carbonyl groups form a six-member ring structure through H-bonding interaction. The energy minimum conformation of the enol form was calculated by a semiempirical (AM1) method using a Gaussian98 program to be a planar conjugated and rigid structure of the whole molecule (Scheme S-2 in Supplementary materials). One hydroxyl group is adjacent to the *N*,*N*-dimethylaniline donor (Scheme 2). These lead to a strong fluorescence emission. In other words, the fluorescence was switched to 'ON' state in *cis*-enol form. In the keto form, two carbonyl groups are relatively free due to the rotation of carbon–carbon bonds. The energy minimum conformation of the keto form displays a dihedral angle of 53.3° between the two carbonyl groups (Scheme S-2), and the whole molecule no longer has rigid and conjugated structure. One carbonyl group is adjacent to the *N*,*N*-dimethylaniline donor. These lead to the fluorescence quenching through the intramolecular free rotation and the n–π* excited state of carbonyl groups. The fluorescence was switched to 'OFF' state in keto form. With UV irradiation, the photoinduced ketonization occurred, and the enol form was converted into the keto form. The fluorescence emission was switched from 'ON' to 'OFF'.

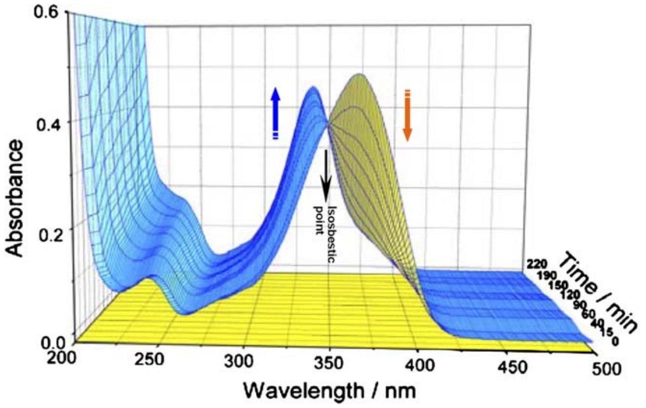


Figure 2. UV–vis absorption spectra of β-diketone **1** in acetonitrile during UV irradiation. Irradiation time: 0, 15, 40, 60, 90, 120, 150, 190, 220 min. Concentration: 2.0×10^{-5} M.

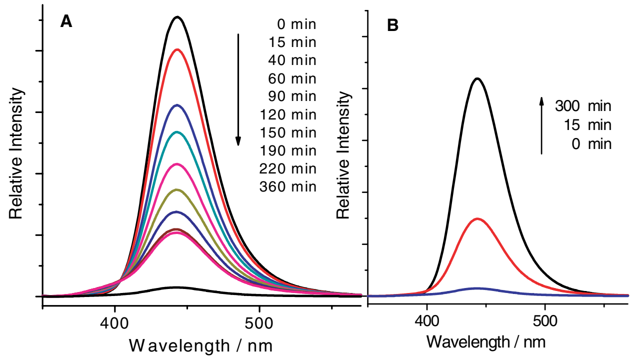
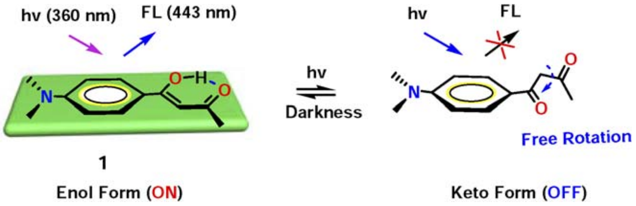


Figure 3. Fluorescence spectra of β-diketone **1** in acetonitrile during UV irradiation (A) from top: 0, 15, 40, 60, 90, 120, 150, 190, 220, 360 min; and in darkness (B) from bottom: 0, 15, 300 min. $\lambda_{ex} = 360$ nm. Concentration: 2.0×10^{-5} M.

According to the UV absorption and emission wavelengths of β-diketones and AM1 semiempirical calculation, the energy level diagrams of enol and keto forms were established for the β-diketone 1. The energy transition pathways of keto and enol forms are illustrated in Supplementary materials (Scheme S-3). In the enol form, the lowest excited state (^{1}π–π*, 365 nm, 3.08 eV) is localized at aromatic donors, strong emission was observed at 443 nm. In ketone form, the lowest excited state (^{3}n–π*, 352 nm, 3.20 eV) is localized at the two carbonyl groups, which is lower than the excited singlet state (^{1}π–π*, 337 nm, 3.34 eV), thus, no fluorescence was observed due to the intersystem crossing (excited singlet state → excited triplet state) according to Lakowicz.[22]

This photoinduced ketonization process is reversible. The keto form can be converted back into the *cis*-enol form in darkness.[6,17] The fluorescence was restored in darkness as shown in Figure 3B. Thus, the fluorescence was switched reversibly from 'OFF' to 'ON' state. The same result was also observed for β-diketone **2**.



Scheme 2. Schematic representation for the reversible fluorescence ON/OFF of β-diketone **1** based on the keto-enol tautomerization.

Such reversible photochemical and photophysical properties at a molecular level may be of great significance in designing new optoelectronic materials and devices. Recently, several classes of molecular switches such as pyrazoline, anthracene, and crown ether derivatives have been reported.[18–20] Cumpston et al. demonstrated high-density optical storage-memory techniques based on fluorescence bits read-out and recording.[21] Their data storage is inerasable due to irreversible fluorescence behavior. According to our results, the reversible fluorescence behavior based on keto-enol tautomerism may provide a fascinating opportunity in designing a novel class of molecular switches and exploring erasable data storage devices.

In summary, saturated β-diketones (**1** and **2**), and unsaturated β-diketone ($A_{(=)}$–D **3**) bearing aromatic amine donors were found to have both keto and *cis*-enol forms in a solution. The enol is the predominant form in a solution as revealed by NMR spectroscopy. In contrast, the novel β-triketone **4** exists in only one enol form in the solution. The saturated β-diketones **1** and **2** display a strong fluorescence, however, almost no fluorescence was observed for the unsaturated β-diketone $A_{(=)}$–D **3**. Reversible photoinduced ketonization of these β-diketones was observed. The fluorescence intensities decreased gradually during photoinduced ketonization. Based on the reversible keto-enol tautomerization, the fluorescence emission was reversibly switched between the 'ON' state in *cis*-enol form, and the 'OFF' state in keto form. Such reversible photochemical and photophysical properties at a molecular level may provide an opportunity in designing a novel class of molecular switches and devices.

Acknowledgments

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Supplementary data

Synthesis and spectroscopic data of **1**, **2**, **3**, and **4**; ^{1}H NMR spectra of **2** and **3** in $CDCl_3$; ^{1}H NMR spectrum of **2** in $CDCl_3$ after UV irradiation (60 min); TGA/DTA curves of **1** and **3**; schematic representation for the thermal behavior of **3**; absorption spectrum of **4** in acetonitrile; schematic representation for the energy minimum conformations of the enol and keto forms of **1** and **3**; energy level diagrams of enol and keto forms of **1**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.02.019.

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14. (a) Fluorescence quantum yields (Q) were calculated from the integrated intensity under the emission band (I) using the following equation:

$$Q = Q_{\mathrm{r}} \frac{I}{I_{\mathrm{r}}} \frac{\mathrm{OD_r}}{\mathrm{OD}} \frac{n^2}{n_{\mathrm{r}}^2}$$

where OD is the optical density of the solution at the excitation wavelength, and n is the refractive index. The optical density of the solution for the calculation of quantum yields was less than 0.1 at the excitation wavelength. 9,10-Diphenylanthrene in cyclohexane was used as reference ($Q_r = 0.90$); (b) Eaton, D. F. *Pure. Appl. Chem.* **1988**, *60*, 1107.
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