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Twofold terminal post-functionalization of acetylacetone with hole- and electron-transporting fragments

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ABSTRACT

A modular synthetic methodology has been developed to prepare β-diketones functionalized with hole- and electron-transporting fragments at their two termini. The optical and electrochemical properties of these new β-diketones are also described in detail.

Acetylacetone (acac) derivatives are extremely attractive for organic chemists,[1] for they play a very important role as building blocks for construction of a broad diversity of natural products, including aromatics and heterocycles.[2] At the same time, they are versatile ligands for numerous metallocomplexes.[3] Among them, europium (Eu), terbium (Tb), platinum (Pt) and iridium (Ir) complexes are extensively used as triplet emitters in organic light-emitting diodes (OLEDs) nowadays.[4] In order to improve their charge transporting ability, hole- and electron-transporting fragments have been introduced into the acac platform.[5] For instance, Bazan and coworkers reported a simple single-layer OLED with an external quantum efficiency of 0.08% using the complex tris[1-(*N*-ethyl-carbazolyl)(3,5-hexyloxybenzoyl)methane](phenanthroline)-europium.[5a] Here, the phenanthroline ligand acted as the electron-transporting medium, and an attached carbazole was used for the hole transport. And in 2001, an oxadiazole-functionlized β-diketonate ligand was synthesized and the Tb complex was prepared.[5b] The current density of its OLED increased from 1.3 to 275 mA/cm^2 at a driving voltage of 20 V compared with the unsubstituted terbium tris(acetylacetonate).

In addition, we have developed bifunctional phosphorescent Ir dendrimers with a 'self-host' feature, in which the core acts as the emissive dopant and the dendron plays the same role as the host.[6] In view of the ease of synthesis in a large scale, the heteroleptic green Ir dendrimer with acac as the ancillary ligand was prepared.[7] Nonetheless, the nondoped device gave an efficiency of 25.8 cd/A, lower than that of the corresponding homoleptic dendrimer (34.7 cd/A). Aiming at high performance of the nondoped devices, it is desirable to link acac ligand with carbazole dendrons to further prevent the intermolecular interactions between the emissive cores.

Because of these motivations, the modification of the acac framework becomes intriguing. However, these compounds are usually prepared via the typical Claisen condensation reaction[8] from ketones and esters (Fig. 1, Method A),[5a,c–e] which means tedious multiple synthetic and purified steps when different functional groups are incorporated. Therefore, the development of a modular synthetic methodology will be a keystone for acac derivatives in optoelectronic application, for it is believed to allow flexibility in varying the functionality in molecules with relative ease. In this regard, a series of novel β-diketones, **D$_1$-BCzacac–D$_3$-BCzacac** and **BOXDacac**, were synthesized in a modular fashion. Their photophysical and electrochemical properties are also presented in this study.

As for acac, both α- and γ-positions can be modified.[1] Nevertheless, α-functionalization may affect the basicity and thus the ligation capability to metal ions of acac, and some compounds are unstable.[9] Thus, our basic strategy is based on the direct post-functionalization of acac at its γ-positions (Fig. 1, Method B). As indicated in Figure 1, γ-alkylation[1] is used to prepare the key intermediate **RG-acac-RG** with two functionalities at its termini, which can further react with hole- and electron-transporting fragments. As a result, such functional entities and the acac skeleton are combined via non-conjugated bond so as to weaken the electronic coupling between them, and thus ensure their relative independence, which is a favorable feature for optoelectronic materials.

It is known that monoalkylations[10] of dipotassioacetylacetone with molecular equivalents of alkyl halides in liquid ammonia are accompanied by appreciable amounts of dialkylation, whereas those of disodio- and dilithioacetylacetone are not.[11] However, two successive monoalkylic reactions can provide dialkylic products through dianions, such as disodio salts.[12] This discovery promotes us to attempt the one-pot dialkylation of acac via trianions.[13] To this end, we first explored the synthesis of **1** by a similar route (Scheme 1). After treatment of acac with 1 equiv NaH and 2 equiv *n*-BuLi, trianion **acac^{3-}** was formed, and then reacted with 2 equiv butyl bromide to successfully afford bialkylic product **1** in a moderate yield of 31%. It is worthy noting that, during the reaction,

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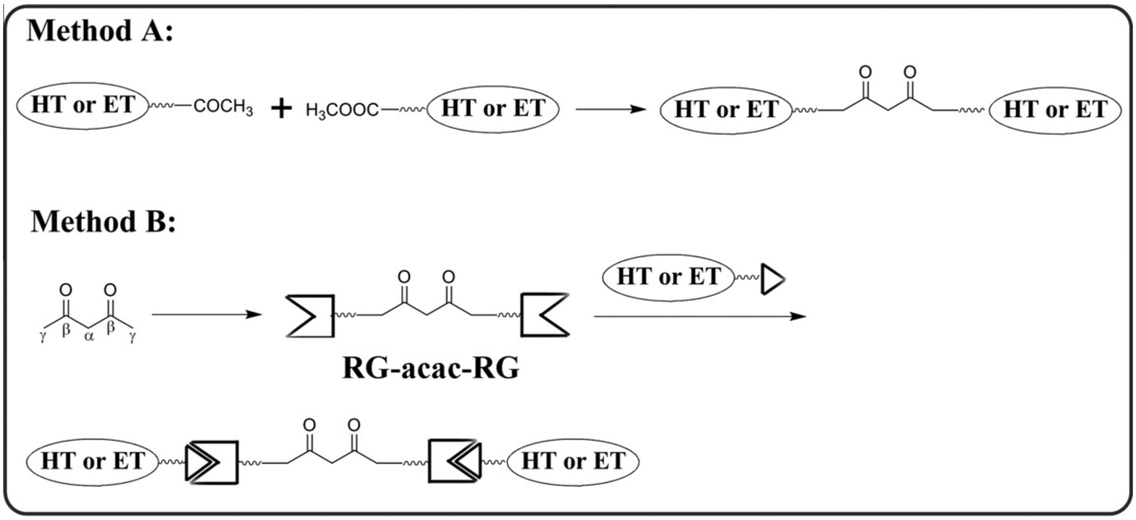
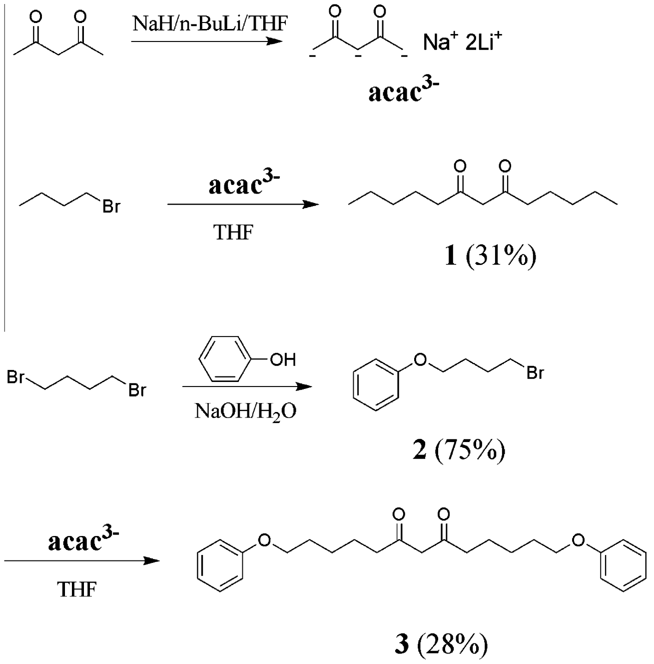


Figure 1. The synthetic routes of β-diketones containing hole- and electron-transporting moieties via the typical Claisen condensation (Method A) and direct post-functionalization (Method B). HT: hole-transporting moiety; ET: electron-transporting moiety.



Scheme 1. Dialkylation of acetylacetone with alkyl bromides.

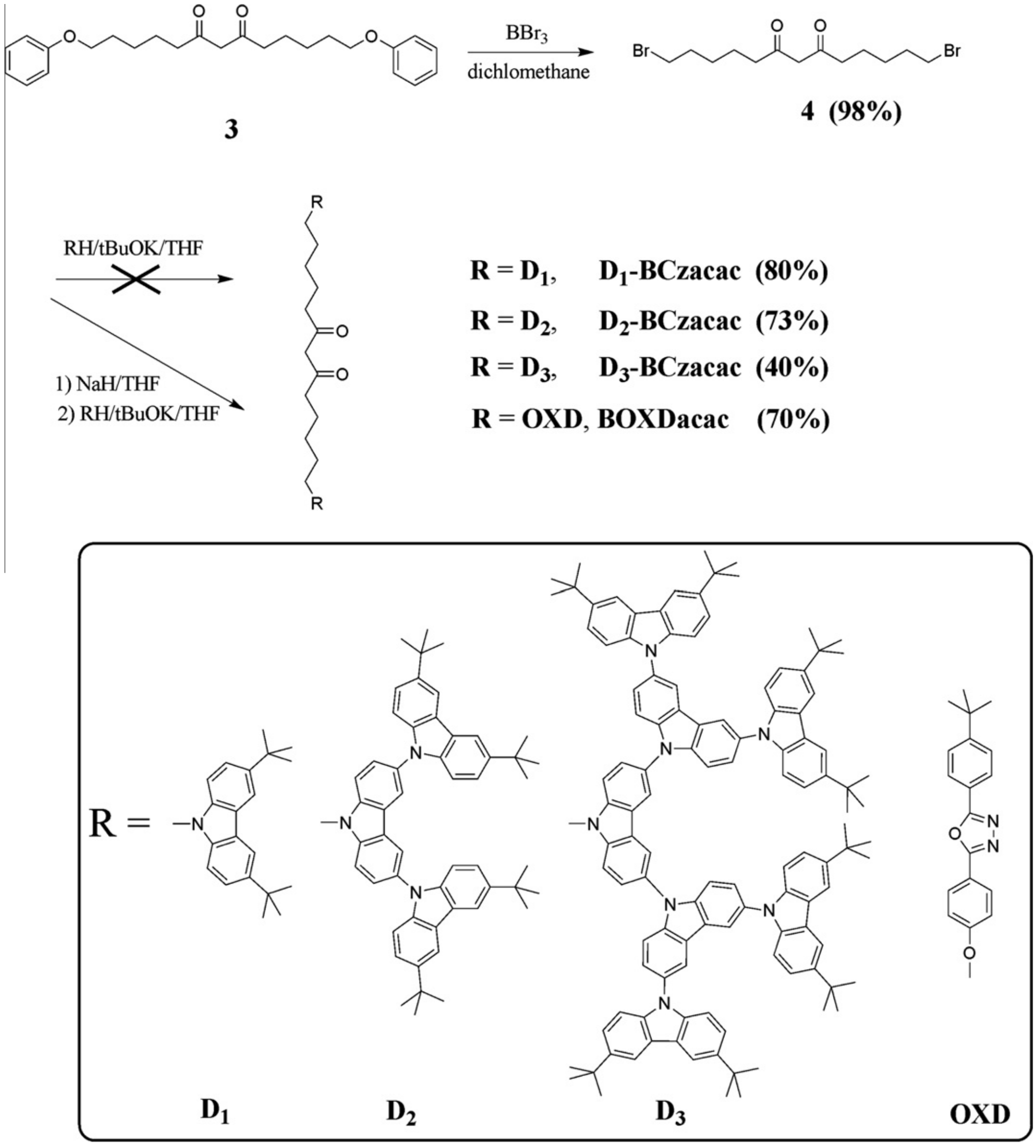
monoalkylic compound was also accompanied, but **1** could be readily separated by distillation under reduced pressure.

Next, we extended this one-pot reaction to synthesize the bromo-substituent target molecule **4**. To avoid the formation of the by-products, 1,4-dibromobutane was protected by phenol at one terminus to give the molecule **2** (Scheme 1). Then reactions were carried out between **2** and the trianion of acac prepared according to the same procedure as **1** to obtain **3** with a yield of 28%. Notably, **3** is a solid at room temperature, whose melting point is about 63 °C, and can be easily isolated from the monoalkylic compound by use of recrystallization along with flash chromatography. Quantitatively, **3** could be converted to **4** in the presence of BBr_3.[14]

Unfortunately, the followed functionalization directly using **4** as the electrophilic reagent failed. This was probably due to the reactivity of acac moiety under the basic conditions. Therefore, an alternative strategy investigated was the adoption of the corresponding monosodio salt instead of **4**, which was obtained by the addition of **4** to 1 equiv NaH in THF solution. Based on the standard nucleophilic substitution conditions,[15] as presented in Scheme 2, we succeeded in performing the reactions of the monosodio salt of **4** with the first, second and third generation carbazole dendrons to provide **D_1-BCzacac** (80%), **D_2-BCzacac** (73%) and **D_3-BCzacac**(40%), respectively. Likewise, **BOXDacac** bearing electron-transporting oxadiazole unit was achieved by Williamson ether reaction[16] in a yield of 70%.

Structures of **D_1-BCzacac–D_3-BCzacac** and **BOXDacac** were confirmed by ^1H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis. From their ^1H NMR spectra, all the synthesized compounds show the characteristic enolic proton absorptions located at around δ 15.42–15.55 ppm. Moreover, the signals appeared at δ 5.34–5.52 and 3.44–3.60 ppm can be ascribed to the α-position protons in enol and keto forms, respectively. By comparing the integration of δ 5.34–5.52 with 3.44–3.60 ppm,[17] the relative ratios of the enol tautomer can be estimated to be more than 80%. This indicates that β-diketones are predominantly enolized in most organic solvents, which is in accordance with the literature.[18]

Absorption and emission spectra of **D1-BCzacac–D3-BCzacac** with respect to the corresponding carbazole dendrons were recorded in dichloromethane (Fig. 2), and the spectral characteristics are summarized in Table S1 (Supplementary data). As for **D1-BCzacac**, the intensity of the absorption band at 268 nm is significantly higher than that of **D1**. This is understandable, for the acac fragment exhibits absorption property with λ_{max} around 270 nm (Fig. S1, Supplementary data). Furthermore, it is noteworthy that the lowest-energy absorption band in the range of 310–370 nm is red-shifted by about 14 nm from **D_1** to **D_1-BCzacac**. Correspondingly, a red shift of 4 nm for the emission maximum is observed accompanied by the spectral broadening. These observations illustrate that the aggregation exists in **D_1-BCzacac**, which may result from the intermolecular hydrogen bonds. As discussed above, the enol tautomer is the predominant form in solutions. Consequently, intra- and intermolecular hydrogen bonds can be formed, between which the intermolecular hydrogen bonds are further able to induce the aggregation of the carbazole dendrons at the focal points. Similar phenomenon has been found previously that hydrogen bonding in 1,3-diketones has effect on crystal packing processes by the formation of so-called 'beta-chains'.[19] Interestingly, this aggregation effect can be completely prohibited when the size of the attached dendron increases. As evidenced by **D_3-BCzacac**, the



Scheme 2. Synthesis of β-diketones functionalized with hole- and electron-transporting moieties.

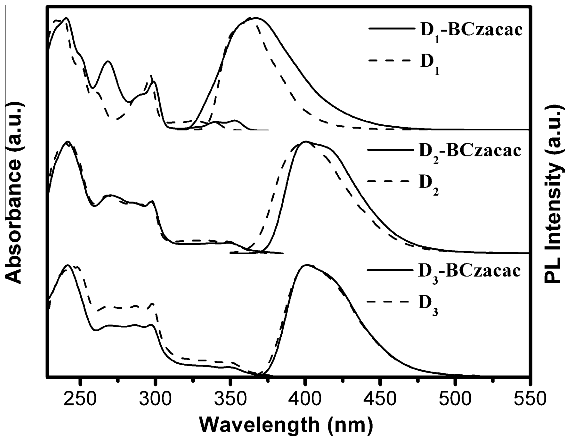


Figure 2. The absorption and photoluminescence spectra of **D_1-BCzacac**–**D_3-BCzacac** compared with the corresponding carbazole dendrons (10^{-5} M in CH_2Cl_2 solution).

absorption and emission spectra are almost identical to those of **D_3**. This is well correlated to the downfield shift of the enolic proton. For example, its chemical shift gradually increases from 15.42 ppm of **D_1-BCzacac** to 15.55 ppm of **D_3-BCzacac**, indicative of the disrupted intermolecular hydrogen bonds with the increasing generation number.[17]

When going from **D_1-BCzacac** to **D_2-BCzacac**, both the absorption onsets and the emission maxima display an obvious bathochromic shift, owing to the enlargement of the conjugation length. As listed in Table S1 (Supplementary data), the optical band gap taken from the absorption onset decreases from 3.42 eV of **D_1-BCzacac** to 3.14 eV of **D_2-BCzacac**, and the emission maximum is red-shifted by about 33 nm. In contrast, from **D_2-BCzacac** to **D_3-BCzacac** this bathochromic effect is almost negligible, and both the absorption and photoluminescence (PL) spectra of **D_3-BCzacac** are nearly the same as those of **D_2-BCzacac**. The results demonstrate that the delocalization of the electronic states is mainly limited to the second generation carbazole dendrons, and does not extend obviously to the third generation ones.

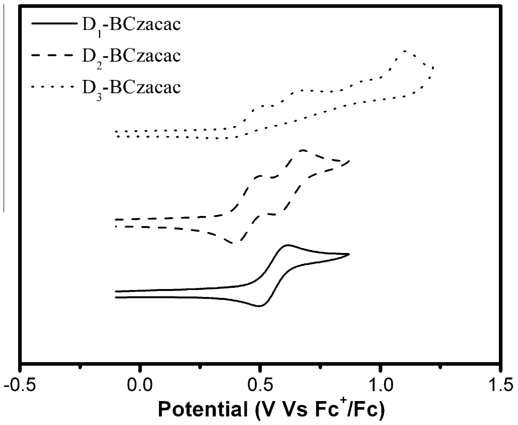


Figure 3. Cyclic voltammograms of compounds **D_1-BCzacac**–**D_3-BCzacac**. Measured in dichloromethane (5.0×10^{-4} M). Scan rate: 100 mV s^{-1}.

The dependence of the conjugation length on the generation number[20] also affects their electrochemical properties. The electrochemical properties of these materials in CH_2Cl_2 (5.0×10^{-4} M) were studied in a three-electrode electrochemical cell with Bu_4NClO_4 (0.1 M) electrolyte, Pt wire counter electrode and Ag/AgCl reference electrode. Due to the different chemical environment of the N-heterocycles in the carbazole units, **D1-BCzacac** show only one reversible redox wave while **D2-BCzacac** and **D3-BCzacac** displayed multi-redox waves. As shown in Figure 3, **D1-BCzacac** and **D2-BCzacac** show reversible oxidation waves with an onset potential of 0.48 and 0.38 V, respectively. And for **D3-BCzacac**, multiple irreversible oxidation peaks together with an onset of 0.39 V are observed. Upon going from **D1-BCzacac** to **D2-BCzacac** and **D3-BCzacac**, we note that, the onset potential firstly moves towards a negative direction, and then remains unchanged. This variation is corresponding to the extension of the π-conjugation with the increasing generation number. In comparison to **D1-BCzacac**, the HOMO energy levels for **D2-BCzacac** and **D3-BCzacac** was enhanced by about 0.1 eV, indicating the lower hole-injection barrier.

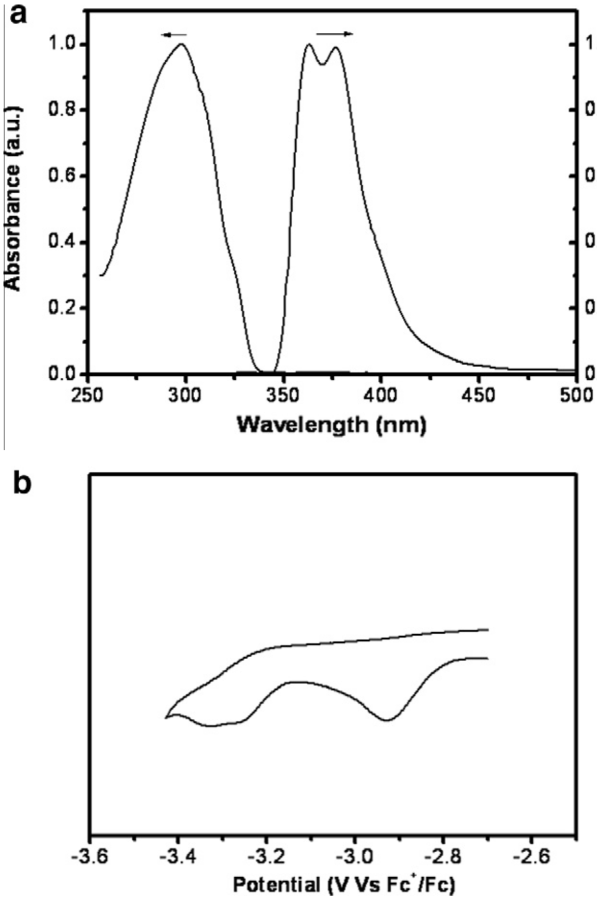


Figure 4. The photophysical and electrochemical spectra of **BOXDacac** (a). Measured in CH_2Cl_2 at a concentration of 10^{-5} M. (b) Measured in acetonitrile (scan rate = 100 mV s^{-1}.

Simultaneously, the photophysical and electrochemical properties of **BOXDacac** were investigated in dichloromethane and acetonitrile. As indicated in Figure 4, **BOXDacac** shows a major absorption band at 298 nm and a maximum emission peak at 363 nm together with a high optical band gap of 3.70 eV. During anodic and cathodic scans, only irreversible reduction waves were found (Fig. 4). Based on the onset of the reduction potential (−2.81 V), its LUMO energy level was calculated to be −1.99 eV. And combined with the optical band gap, the HOMO energy level could be estimated to be −5.69 eV.

In summary, we report a modular synthesis of novel β-diketones containing hole-transporting carbazole dendrons and electron-transporting oxadiazole units. In solutions, the enol tautomer is the predominant form, and the formed intermolecular hydrogen bonds can cause the aggregation of the carbazole dendrons at the focal points. With increasing generation number, however, the aggregation effect can be entirely suppressed. Further incorporation of these compounds as the ancillary ligands for the Ir complexes in optoelectronic application is currently under way in our laboratory.

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Supplementary data

Supplementary data (synthetic details and spectroscopic characterizations for new compounds) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.06.090.

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