Heterocyclic Radical Mediated Synthesis and Fluorescence Properties of Conjugated Polyene Ketones
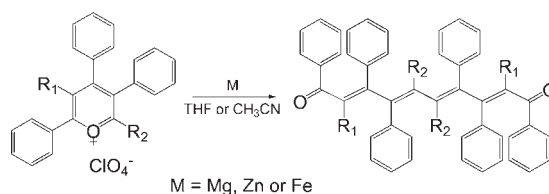
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ABSTRACT

A straightforward route for the preparation of decatetraene diketone derivates is presented. The synthesis has been accomplished by a one-step procedure starting from phenyl-substituted pyrylium perchlorates, and an elaborate heterocyclic α-radical mechanism was proposed. This class of molecules displays a crystallization induced emission enhancement property.

A great deal of conjugated polyene derivatives with tunable geometry[1] and electro-optical properties,[2] are among the most important linear chemical structures that have found application in organic light-emitting diodes (OLEDs), photovoltaic cells, lasers, field-effect transistors (FET), molecular wires, and fluorescent tags.[3]

Nonetheless, synthesis of conjugated polyene derivatives usually requires redundant synthetic approaches.[4] For example, the building blocks trienes and tetraenes were synthesized usually by Stille coupling reactions involving the use of toxic organometallic reagents and multiple Sn/Li exchange processes, which is a concern to human health and the environment.[5] Terminal-functionalized polyenes were synthesized by Pd-catalyzed cross-coupling reactions with more than three synthetic steps besides additional modification reactions for each reactant.[6] The polyenes containing up to 15 double bonds were fabricated by a coupling reaction of ketenes and organomolybdenum reactants, which were synthesized by multistep organometallic reactions under rigorously controlled reaction conditions.[7] As important heterocyclic compounds and synthetic organic intermediates, pyrylium salts were

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well-known for their nucleophilic reactions at the C-2/6 site for the subsequent Claisen rearrangement.[8] Herein we would like to report the synthesis of decatetraene diketone derivatives with six adjacent double bonds which employed a one-step reaction, via the carefully designed pyran-α-radical intermediates. Their crystallization-induced emission enhancement (CIEE) properties correlating to their inherent intramolecular interactions were investigated.

Pyrylium salts with a positive formal charge located on oxygen (actually in all reactions the positive charge is located on C-2/6 and C-4 sites) prefer nucleophilic addition at the C-2/6 or C-4 site to allow the synthesis of useful organic compounds.[9] Metal reduction of pyrylium salts was reported to generate pyran-radicals only at the C-4 site leading to pyran-4,4′-dimers[10] (Scheme 1, **2a−b**). It is well-known that nucleophilic reaction of pyrylium cations at the C-2/6 site could give abundant organic compounds for the subsequent Claisen rearrangement, compared with that at the C-4 site leading to the final products without any further structure variation. Therefore, developing a pyran-α-radical (radical at C-2/6 site) would be valuable for filling in the vacancy of heterocyclic radical reactions at the C-2/6 site and the synthesis of compounds with interesting electro-optical properties. Taking into account the references concerning metal reduction of pyrylium salts,[10] the pyran-4,4′-dimer dominated conversions were speculated to deviate from the nature of pyrylium. It is believed that the pyran-α-radicals could be generated by metal reduction of pyrylium cations.

To confirm this hypothesis, metal reduction of pyrylium salts was initiated after establishing the reaction conditions. The solvent mixture (which was found to have an important impact on the reaction selectivity) of water/ether[11] (or acid−water/benzene[12]) was replaced by THF, since the reactant pyrylium could dissolve in refluxing THF and lead to an accelerated reduction process. When the reaction finished, the reactant could be isolated by filtration together with metal. Then the products could be purified just by evaporation under reduced pressure and recrystallization. The reaction temperature was up to the solvent refluxing point. When stirring for hours with zinc reduction, the products **3a** and **3b** were obtained and

purified by recrystallization in methanol. The characterization results imply the reduction generates a radical center localized at C-6 on pyrylium cations to fabricate pyran-dimers.

Scheme 1. Dimerizations of **1a−b**[a]
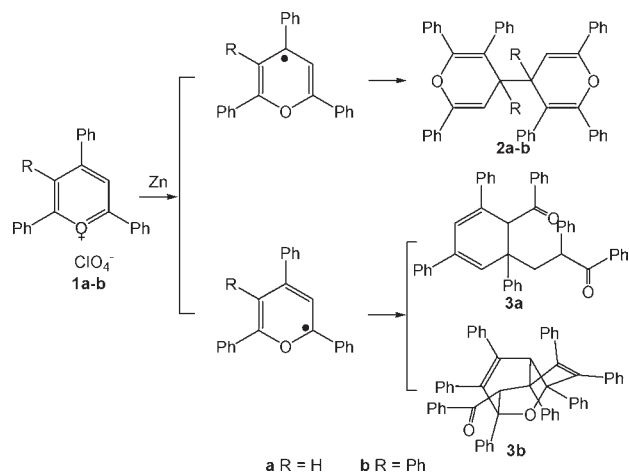
[a] For synthesis of **2a−b** mediated by pyran-γ-radicals[10b,f,11] and synthesis of **3a−b** mediated by pyran-α-radicals, respectively.

The MS, ^{1}H NMR, ^{13}C NMR and X-ray singe crystal analysis allowed the identification of their geometries (Figure S1). The crystals of these products were synthesized in layered CH_2Cl_2/CH_3OH with diffusion method. The molecular structures of **3a** and **3b** are proposed to be formed by complication transformations including Claisen rearrangement and Diels−Alder addition following the dimerization of pyran-α-radicals. The proposed mechanism (Supporting Information (SI), Scheme S1) has implied the potential for large-scale synthesis by metal reduction of pyrylium cations at C-2/6 sites.

Scheme 2. Synthesis of **6a−c** from **4a−c**
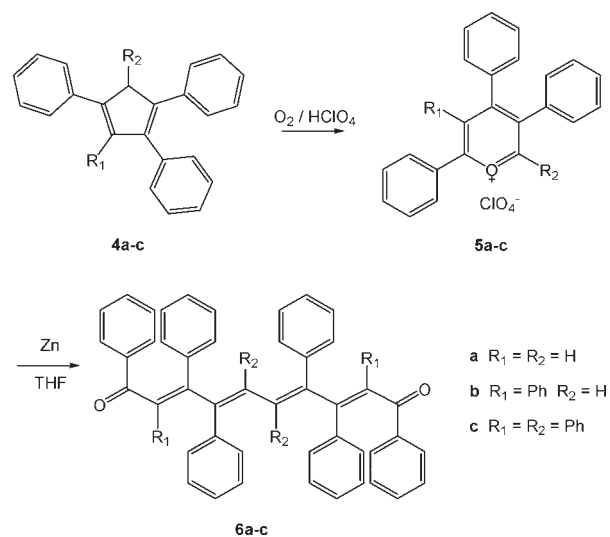
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To further study the dimerization of pyrylium salts mediated by a pyran-α-radical, metal reduction of **5a−c** had been carried out. Pyrylium salts **5a−c** with less sterically hindered C-6 sites were synthesized (SI, Figure S2) via a ring-expanding reaction of **4a−c** according to our previous reports.[13] Under the same conditions, the pyrylium salts were converted into a series of decatetraene diketone derivatives by the metal reduction approach (Scheme 2).

To achieve optimized reaction conditions leading to clear conversion with complete specificity, arrayed comparison tests were carried out. With the reaction temperature decreased to 40 °C without other adjustments, the reaction had finished in a comparatively longer time, which indicates temperature plays a dynamic factor in influencing the reaction process. The solvent could be replaced by acetonitrile without any significant effects except for an inverse reaction phenomenon, in which the reaction systems were solutions (except metal powders) at the beginning and were suspensions when the reaction finished.

Table 1. Different Reductants Comparison on **5a**[a]

| entry	reductant	ratio [vs pyrylium]	reaction times [h]	yields [%]
1	Mg	3:1	5	71.2
2	Zn	3:1	5	70.8
3	Al	5:1	12	−
4	Fe	5:1	8	52.3

[a] Reaction conditions: THF, refluxing.

Ether was run with similar reaction conditions, achieving reaction inhibition under refluxing. It is probably attributed to the insolubility of pyrylium salts. The reductant Zn was considered to react at a stoichiometric ratio with respect to pyrylium salts, which meant pyran-radicals were generated in equal with donated electrons. Other reductants including Mg, Zn, Fe, and Al were evaluated, and the results were summarized in Table 1. Except for Al showing no conversion (entry 3), probably due to the generated film shielding metal particles, other metal reductive capabilities are in accord with the corresponding reductive activity and conversions. Real-time monitoring of HPLC illustrated that the absence of oxygen is crucial for reaction conversions. This is ascribed to the partial quenching reaction of intermediate pyran-radicals with oxygen to generate multiple unknown products rather than attaching to another to produce their dimers, so N_2-bubbling into system occurred throughout the reaction process. The simple reaction mechanism was proposed that double Claisen rearrangements follow the dimerization of pyran-α-radicals which are generated by metal reduction of pyrylium salts, finally providing decatetraene diketones (Scheme 3).

The structures of dimers were determined as decatetraene diketones. The pictured crystal structures as shown

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Scheme 3. Proposed Mechanism of Pyran-α-radicals Mediated Dimerization
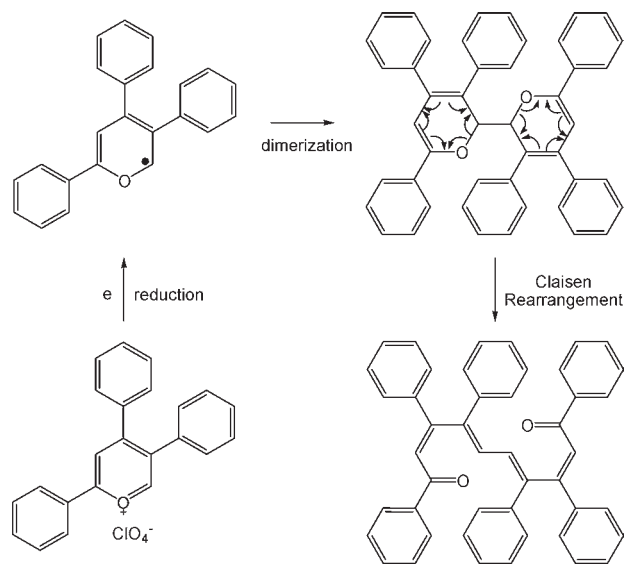

(Figure 1) indicate that steric hindrance affects skeleton structures directly. In **6a** the relatively low steric hindrance leads the decatetraene diketone skeleton to be fabricated in the form of symmetric two helix chain units binding at C1−C1A. The freely arrayed phenyl substituents cause significant C−H···π intramolecular interactions, which
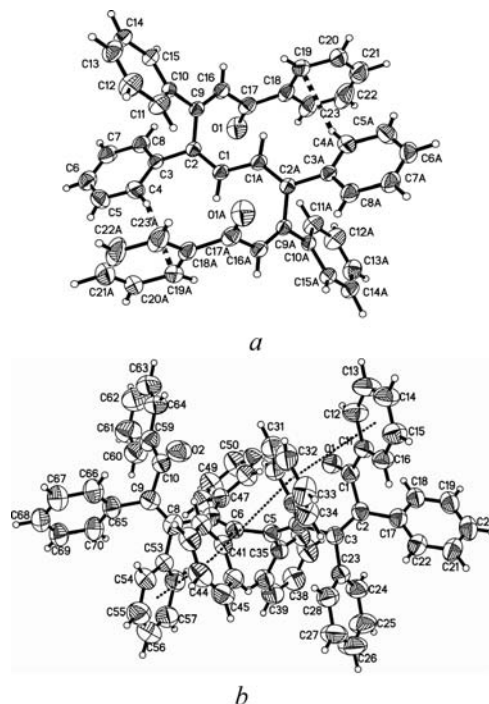
Figure 1. ORTEP view (ellipsoid at 30% probability level) of **6a** (a) and **6c** (b) with intramolecular interactions (dashed lines are C−H···π interactionin and *J*-aggregated phenyl groups).

are similar to the *T*-aggregation mode of aromatic compounds to readily constitute their crystals. When phenyl substituents are added as in **6c**, the steric hindrance forces dense substituents parallel-aligning just as in the *J*-aggregation mode fixing the molecular geometry. And the C−H···π interaction is absent for there is not enough space for its proper bond angle. These abundant intramolecular interactions affect molecular geometries as well as induce unique properties. Detection of the fluorescence of these decatetraene ketones showed they emit nearly the same green fluorescence emissions in the aggregation state (around 515 nm of emission wavelengths, Table S1) but barely detectable emissions in solution, which is the so-called property of crystallization-induced emission enhancement (CIEE).[14] Especially for **6b**, fluorescence
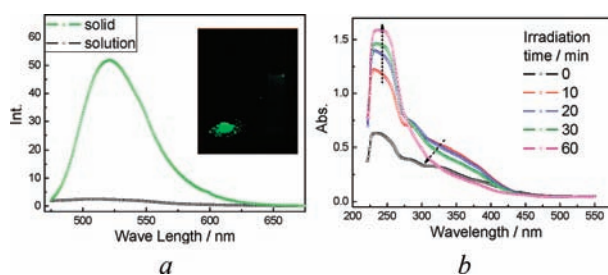
Figure 2. (a) Emission spectra and photographs (insert) of **6b** in crystal state and solution. (b) The UV−vis absorption spectra of **6b** solution with different UV (λ_{max} = 365 nm) irradiation times. The solution is 10^{-4} M of **6b** in CH_2Cl_2.

emission from its crystal is over two hundred times more intensive than from its 10^{-4} M solution of CH_2Cl_2 (Figure 2a), and the fluorescence quantum efficiency increases by about 100 times (Φ_F is just 0.004 in solution but 0.411 in crystal state), too. It is suggested that in the stacking mode the irregular molecular conformations make the intermolecular distances enlarge, while the intramolecular

interactions stabilize molecular geometries. Together with the rigid structures consisting of multiple π bonds in backbones termed chromophores, they lead to the result that all decatetraene diketones deliver intensive fluorescence emissions in the crystal state. Then in CH_2Cl_2, the solution molecules have a considerable impact on intramolecular interactions and make the solute molecular conformations flexible; namely, the long conjugated ketene backbones could easily twist. The increase of nonradiative decay pathways maybe consume the excitation energy and induce fluorescence emissions quenching. The latter UV−vis absorption detections (Figure 2b) for their solutions showed that the absorption curves continuously changed during exposure to the UV lamp (365 nm wavelength). The B-bonds absorption around the 350 nm wavelength relatively decreases while K-bonds absorption persists or increases as the irradiation time was prolonged (except for the initial irradiation variation), which indicates destruction of the rigid molecular geometries and conservation of small structure moieties such as rigid conjugated styrene segments. When the UV lamp was removed, the compounds recovered their original dominant geometries. These results demonstrated our ratiocination regarding their flexible skeleton structures in solution.

In summary, we have developed a one-pot synthetic method for decatetraene diketone derivates via a pyranyl-α-radicals predominated dimerization. The relationship between crystal structures and emission properties was carefully studied. This method may have its greatest value beyond the formation of conjugated polyenes from cyclopentadiene derivatives. Further studies on heterocyclic radical mediated dimerizations are expanded to other heterocyclic salts to fabricate functional conjugated polyenes.

Supporting Information Available. X-ray crystallography and optical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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