Tetrahedron Letters 54 (2013) 2967–2971

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Highly efficient one-pot synthesis of α-free pyrylium salts with tunable fluorescence emission via ring-expanding reaction of triarylcyclopentadienes

Lijian Yang, Junwei Ye *, Yuan Gao, Dai Deng, Weitao Gong, Yuan Lin, Guiling Ning *

State Key Laboratory of Fine Chemicals and School of Chemical Engineering, Dalian University of Technology, Dalian 116012, PR China

ARTICLE INFO

Article history:
Received 5 January 2013
Revised 11 March 2013
Accepted 25 March 2013
Available online 6 April 2013

Keywords:
α-Free pyrylium perchlorates
Fluorescence
Crystal structure
DFT calculation

ABSTRACT

A series of α-free pyrylium perchlorates were prepared by one-pot oxidation of substituted cyclopentadiene derivatives in the presence of perchloric acid. A tunable fluorescence with green to red emission in dichloromethane and green to orange emission in the solid state can be achieved by changing the aryl groups on 2- or 4-position of pyrylium ring. Furthermore, single crystal structures and quantum chemistry calculation were conducted to understand the relationship between structures and optical properties.

Organic fluorescent materials have received considerable attention in both scientific research and practical aspects because of their promising applications in electronic and photonic devices.[1] For expansion of fluorescence-based applications, particularly in fields of organic light-emitting diodes and molecular probes, controlling emission properties of organic fluorophores has become a hot research topic. So far, many approaches have been explored to tune the emission wavelength of organic molecules in solution, such as utilizing of exogenous additives[2a–c] and linking small molecules with macromolecule backbone.[2d,e] In contrast, only a few studies have been reported to tune emission properties of luminescent molecules in the solid state.[3] As an important type of heterocyclic luminescent compounds, pyrylium salts are used in many fields such as organic intermediates,[4a–c] photosensitizers,[4d,e] Q-switchers,[4f] laser dyes[4g] and organic luminophores.[4h] Recently, many studies have been conducted to optimize the photophysical and electrochemical behavior of pyrylium salts. For example, the introduction of different electron-withdrawing or -donating substituents on pyrylium ring varied quantum efficiency and tuned the emission properties.[5] However, these studies are only limited to 2,4,6-tri-substituted-pyrylium salts which are usually obtained by a lengthy stepwise manner hinging on the formation and cyclization of a 1,5-diketone.[6] In our previous work, we developed a high-efficiency one-pot synthesis of pyrylium salts with only one substituent at α position (named α-free pyrylium salts) from polyphenyl–cyclopentadiene compounds in the presence of silver(I) perchlorate or perchloric acid.[7] Much to our surprise, these compounds display unique reactivity to nucleophilic reagents.[8] As a part of our continuous studies on α-free pyrylium salts, we focus on the universality of our synthetic route and the influence of substituents on the optical properties of α-free pyrylium salts. Herein, we report the synthesis of α-free pyrylium perchlorates with tunable fluorescence emission via ring-expanding reaction of triarylcyclopentadienes with different aryl substituent groups. The influence of substituents on the absorption and emission behavior of products was examined by the variation of donor strength and position on pyrylium ring. In addition, single crystal structures and quantum chemistry calculation are conducted to explain the relationship between structures and optical properties.

Cyclopentadiene derivatives were prepared according to the published procedure.[9] Pyrylium salts **2a**–**2g** were synthesized according to our previously reported synthetic route in high yields (Scheme 1).[7b,10] Their structures are well characterized by ^{1}H NMR, ^{13}C NMR, HRMS, MS, and X-ray single-crystal diffraction. The optical properties of **2a**–**2g** were investigated by UV–vis absorption spectroscopy (Fig. 1) and photoluminescence spectroscopy (Figs. 2 and 3) in dilute dichloromethane solution and in the solid state. The maximum absorption wavelengths λ_{max}^{Abs} of these compounds are in the range of 372–457 nm (Table 1), which are caused by π–π* transition of molecular plane. As expected, the λ_{max}^{Abs} of **2a** and **2b** shifted hypochromatically of 18 nm and 4 nm compared with that of Br-substituted **2c** owing to the stronger electron-withdrawing effect of CF_3 and F. Compared with **2c**, the λ_{max}^{Abs} of **2d**–**2g** is bathochromically shifted of 67, 50, 30, and 65 nm, respectively, which is due to the extending conjugation in the backbone and the enhanced charge transfer from the pyrylium O-atom to the electron donating naphthyl, biphenyl, and naphthyl–phenyl groups

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* Corresponding authors. Tel.: +86 411 84986067; fax: +86 411 84986065.
E-mail addresses: junweiye@dlut.edu.cn (J. Ye), ninggl@dlut.edu.cn (G. Ning).

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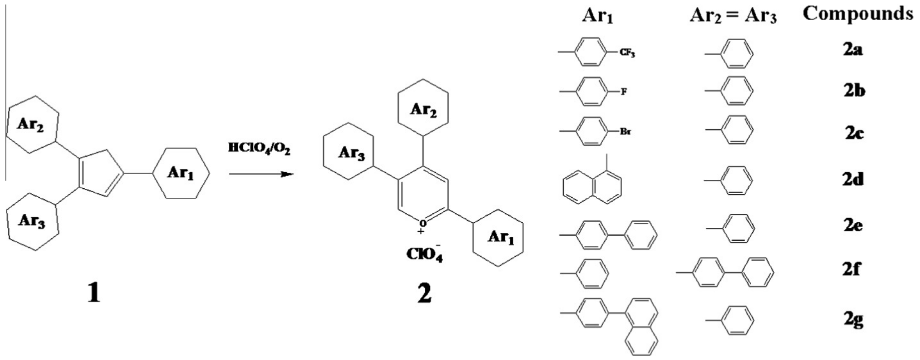
http://dx.doi.org/10.1016/j.tetlet.2013.03.113



Scheme 1. Synthetic route to α-free pyrylium perchlorates from cyclopentadiene derivatives.

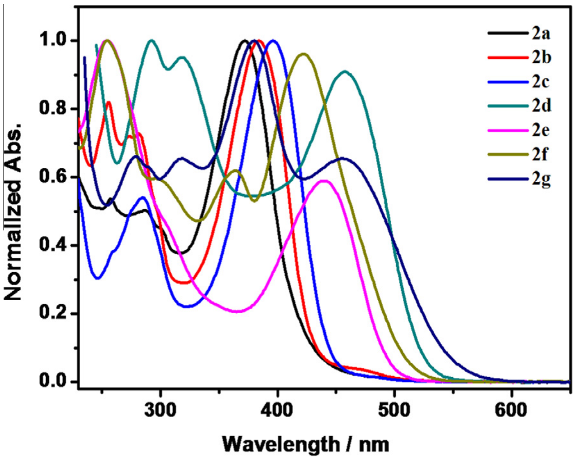


Figure 1. Normalized UV–vis absorption spectra of **2a**–**2g** in dichloromethane at 5×10^{-5} M concentration.

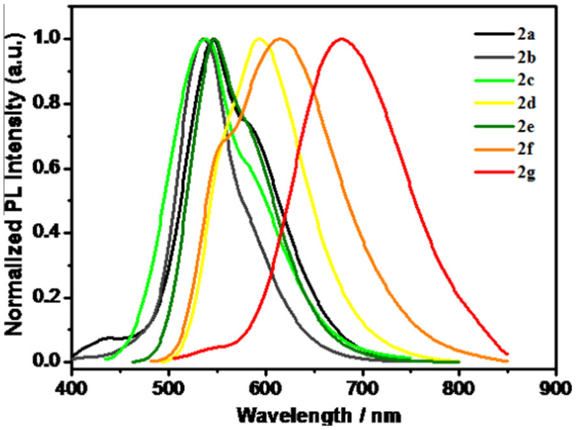


Figure 2. Normalized PL spectra of **2a**–**2g** in dichloromethane at 5×10^{-5} M concentration.

on 2- or 4-position. Compound **2d** possesses the longer wavelength absorption than that of **2e**–**2f,** which may be attributed to the retardation of electronic delocalization in **2e**–**2f** caused by the more twist configurations between the pyrylium ring and α-linked aryl groups. The photoluminescence (PL) spectra of **2a**–**2g** in dilute dichloromethane solution showed emitting peaks at 535–680 nm with light region from green to red (Fig. 2). The fluorescence maximum wavelength of pyrylium salts shifts bathochromically with introducing electron-donating substituents but is weakly influenced by electron-acceptors. For instance, the maximum emitting peaks of **2c**, **2e**, **2d**, and **2g** in dichloromethane solution are 538, 547, 595, and 680 nm, respectively. The PL quantum efficiency (Φ_{FL}) of **2a**–**2g** in dilute dichloromethane solution ranged from 0.0125 to 0.90 (Table 1).

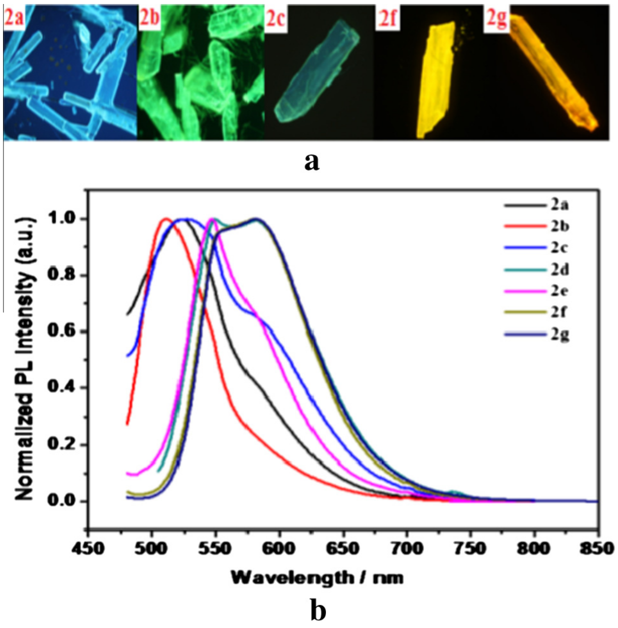


Figure 3. (a) Crystal photographs of compounds **2a**–**2c**, **2f**, and **2g** under the irradiation of UV lamp (365 nm); (b) normalized PL spectra of **2a**–**2g** in the solid state.

Then the fluorescence emission properties of **2a**–**2g** in solid state were measured (Fig. 3). The emission of **2a**–**2g** is in the blue to yellow region with the emission peaks from 469 to 580 nm (Table 1). However, the shapes of PL spectra of **2d**, **2f**, and **2g** are similar, indicating that these emitting bands should be a local emission from the pyrylium fragment. The photographs of crystals **2a**, **2b**, **2c**, **2f**, and **2g** under illumination with UV light (λ_{ex} = 365 nm) are shown in Figure 3a. Pyrylium salts **2a**–**2c** emit strong blue, strong green, and weak yellow–green light, respectively, whereas **2f** and **2g** exhibit yellow emission. To investigate the properties in further detail, the fluorescence quantum efficiency (Φ_{FL}) in solid state was examined as summarized in Table 1. The pyrylium salts **2f** with biphenyl in 4-position exhibit a weak Φ_{FL}, owing to the hindered rotation of single bond in 4-position which is unfavorable for quantum efficiency. In comparison, other pyrylium salts have much

Table 1
Thermal properties, optical properties, and energy levels of α-free pyrylium perchlorates

Compound	T_d/°C	λ_{abs}[a]/nm	λ_{em}[a]/nm	λ_{em}[b]/nm	Φ_{FL}[a]/%	Φ_{FL}[b]/%	ΔE_g^{opt}[c]/eV	E_{LUMO}[d]/eV	E_{HOMO}[e]/eV	ΔE_g^{cal}/eV
2a	215	372	546	469	3.62	28	2.50	−4.33	−1.83	2.28
2b	200	386	536	511	8.40	48	2.48	−4.27	−1.79	2.29
2c	215	390	538	526	7.00	45	2.48	−4.31	−1.83	2.32
2d	215	457	595	550	30.6	39	2.28	−4.25	−1.98	2.04
2e	200	440	547	547	90.0	46	2.39	−4.27	−1.88	2.47
2f	235	421	615	580	4.18	6.0	2.33	−4.29	−1.96	2.21
2g	235	455	680	581	1.25	65	2.16	−4.26	−2.10	1.17

[a] Measured in dichloromethane solution (5×10^{-5} M).
[b] Measured in the solid state.
[c] Bandgaps calculated from absorption edge: $\Delta E_g^{opt} = 1240/\lambda_{onset}$.
[d] The LUMO energy levels were calculated from E_{red} values of CV curves: $E_{LUMO} = -(E_{red} + 4.8)$ eV.
[e] The HOMO energy levels were calculated using the equation: $\Delta E_g = E_{HOMO} - E_{LUMO}$.

higher Φ_{FL} values. Especially, **2g** with naphthyl–phenyl on 2-position exhibits a highest Φ_{FL} value of 65%.

To understand the relationship between molecular structures and optical properties, the crystal structures of **2a**–**2c** and **2g** were determined by single-crystal X-ray diffraction analysis. A summary of the crystallographic data and structure refinements is tabulated in Table S1 while the selected bond lengths and angles are listed in Table S2. The thermal ellipsoid plots and packing diagrams of **2a**–**2c** and **2g** are shown in Figures. 4–7. The asymmetric unit contains an independent pyrylium cation (py+) and a ClO_4^- anion. There are C–H···π and π···π interactions between py+ cations. The distance and the angle of these interactions are tabulated in Table S3. Similar crystal packing structure was observed from compounds **2a**, **2c**, and **2g** indicating the generality of these pyrylium salt molecules. As shown in Figures. 4b, 6b and 7b, the building blocks of these structures are not monomers, but rather the dimers based on the C–H···π interactions between adjacent two molecules. Furthermore, the dimers adopt a stair-like packing mode or a kind of distorted J-type stacking style to form molecular columns. These results suggested the latent relationship between emission properties and crystal structures. Firstly, multiple C–H···π interactions in **2a**–**2c** and **2g** effectively reduce the vibration and rotation of molecules. Secondly, the distorted J-type stacking in **2a**, **2c**, and **2g** effectively avoids the strong intermolecular face-to-face interaction (H-aggregation) which could lead to the formation of an excimer complex and non-radiative relaxation. Thirdly, the large distance between vertical dimers in **2a** (7.73 Å), **2c** (6.98 Å), and **2g** (10.41 Å) makes π···π interaction impossible. Therefore, these

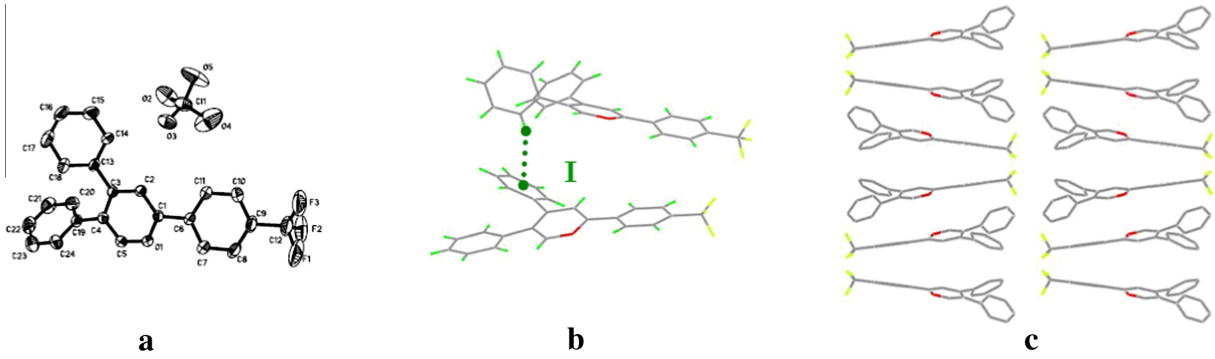


Figure 4. ORTEP drawing with 30% probability thermal ellipsoids (a) and packing arrangements (b and c) of **2a**.

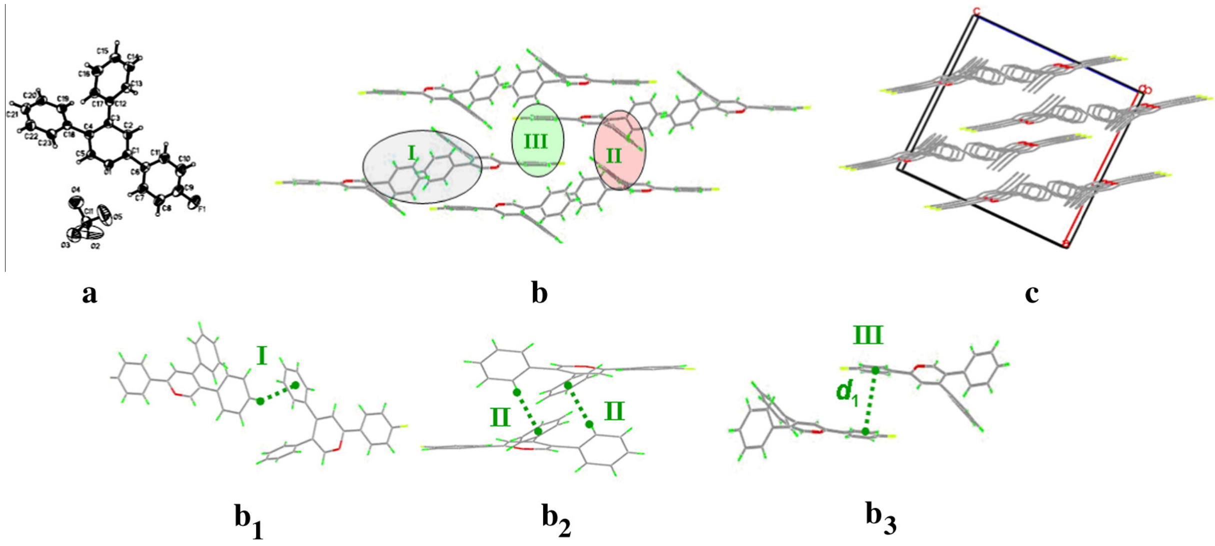


Figure 5. ORTEP drawing with 30% probability thermal ellipsoids (a) and packing arrangements (b and c) of **2b**.

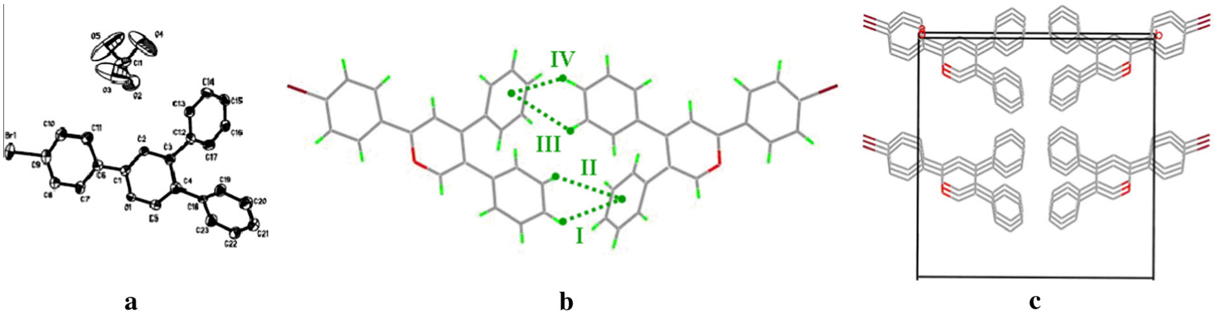


Figure 6. ORTEP drawing with 30% probability thermal ellipsoids (a) and packing arrangements (b and c) of **2c**.

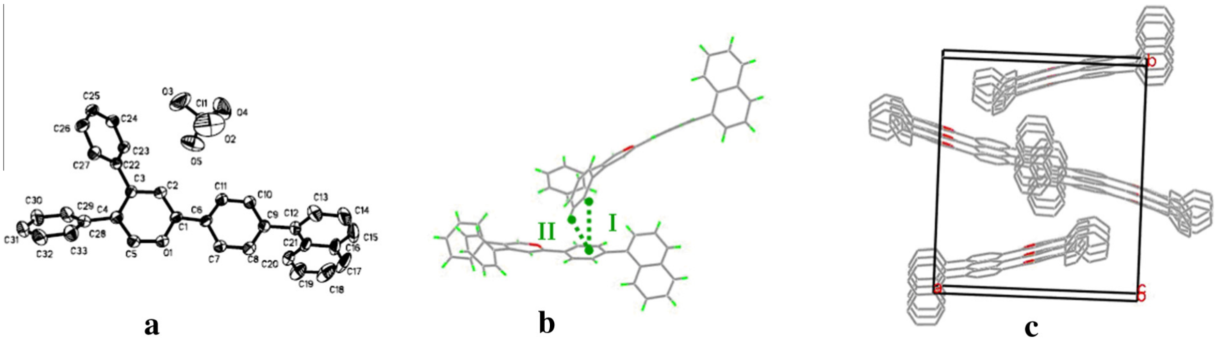


Figure 7. ORTEP drawing with 30% probability thermal ellipsoids (a) and packing arrangements (b and c) of **2g**.

three points may be used to explain the much higher Φ_{FL} values of these compounds in the solid state compared to those in solution.

To further understand the correlation between structures and optical properties, quantum chemistry computation was conducted. The geometries of the molecules have been optimized using DFT calculations with the GAUSSIAN 09 program.[11] The torsion angles collected in DFT calculations and single crystals of **2a**–**2c** and **2g** are tabulated in Table S4, which can be used to explain the blue-shift of emission in the solid state. As shown in Table S4, there are almost no changes of torsion angles between pyrylium ring and aryl groups on 4- and 5-positions. However, the torsion angles between aryl groups on 2-position and pyrylium ring in crystal **2a**–**2c** and **2g** are 12, 27, 10, and 9°, respectively, which are much larger than those in single molecular state (1–2°). Due to the more twisted configuration in the solid state, the maximum emission wavelength occurs with blue-shift compared to that in solution. For **2g**, the blue-shift is 99 nm because the terminal naphthyl in 2-position is twisted out of the pyrylium ring by 67.9°, which greatly decreases the degree of π-conjugation. Electrochemical studies (Fig. S22) were carried out to ascertain the redox behavior of **2a**–**2g.** The ΔE_g^{opt} and energy values of HOMO and LUMO of **2a**–**2g** are shown in Table 1. The HOMO energy values of **2a**–**2g** are from −2.10 to −1.79 eV and the ΔE_g^{opt} values determined from the absorption edge are from 2.16 to 2.50 eV which are similar to the ΔE_g^{cal} (1.17–2.47 eV). Compound **2g** has the lowest ΔE_g^{opt} and ΔE_g^{cal} which is attributed to the better π-conjugation of the 4-(naphthyl)phenyl substituent. Figure 8 shows the optimized geometries and the orbital distributions of HOMO and LUMO energy levels of these compounds. The electron clouds of the HOMOs and LUMOs are dominated by the different parts of

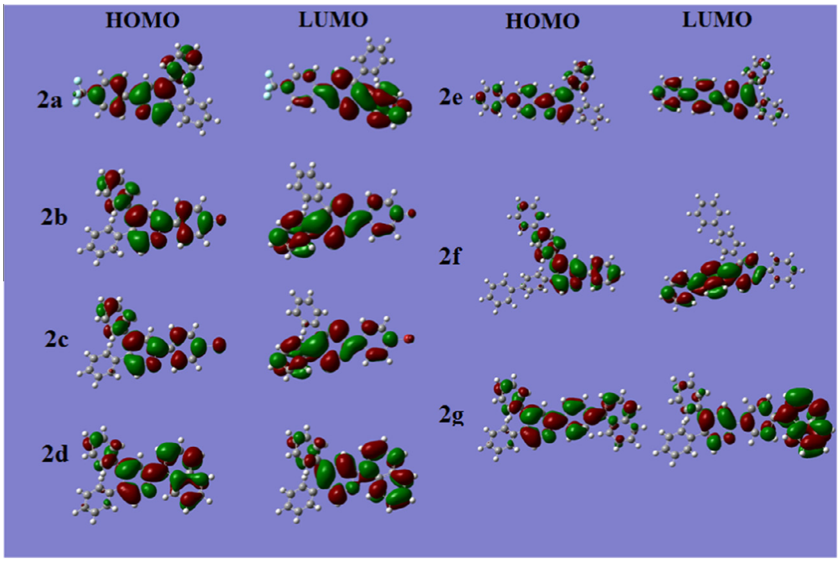


Figure 8. Calculated molecular orbital amplitude plots of HOMO and LUMO levels.

molecules except **2d**, showing the intramolecular charge transfer of these compounds.

In summary, a new class of α-free pyrylium perchlorates was synthesized by one-step oxidation of cyclopentadiene derivatives in the presence of perchloric acid. A tunable fluorescence in solution or in the solid state can be achieved by changing the aryl groups on 2- or 4-position of pyrylium ring. These compounds exhibited maximum emission at 535–680 nm in solution (CH_2Cl_2) and at 469–581 nm in the solid state. Single crystal X-ray diffraction analysis shows that multiple $C–H\cdots\pi$ interactions in **2a**–**2c** and **2g** lead to the much higher Φ_{FL} values in solid states. Electrochemical studies showed the HOMO energy values of **2a**–**2g** were from −2.10 to −1.79 eV and the ΔE_g^{opt} values were from 2.16 to 2.50 eV. This new one-pot synthesis route of pyrylium salts may have great value for synthesis chemistry and materials chemistry. These compounds may be promising candidates as organic luminescent materials.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (51003009 and 20772014), the Specialized Research Fund for the Doctoral Program of Higher Education (200801411121), and the Fundamental Research Funds for the Central Universities of China (DUT11LK16).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.03.113.

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10. *Synthetic procedure for compounds* ***2a*****–*****2g***: a mixture of triarylcyclopentadiene derivative (0.62 mmol) and perchloric acid (70%, 1 mL) in 15 mL toluene/acetonitrile (3/1) was stirred at room temperature. After 1–3 days, 30 mL diethyl ether was poured in this mixture and the precipitate was generated. The flitered precipitate was washed with diethyl ether (3 × 15 mL) and dried to give crude product. The resulting solid was recrystallized from acetic acid for purification.
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