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Efficient cascade reactions for luminescent pyrylium biolabels catalysed by light rare-earth elements†

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Cascade catalysis allows multiple chemical steps to occur in a well-defined sequential manner without the isolation of reaction intermediates, and has been applied for the efficient preparation of natural products, pharmaceuticals and agrochemicals, with the preparation of organic functional dyes having been rarely explored. In the present study, light rare-earth elements are found to catalyse cascade reactions from simple aromatic substrates and acetic anhydride to give luminescent pyrylium salts with yields up to 50% under mild conditions. The cascade reactions have been coupled to supramolecular assembly to form aqueous pyrylium nanoparticles that can function as protein labels.

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Introduction

There is tremendous research interest in the development of efficient methods for high-value chemical transformation from simple substrates.^{1–5} Cascade synthesis, that mimics Nature's chemistry, allows multiple chemical steps to occur in a well-defined sequential manner without the isolation of reaction intermediates.^{6–9} The cascade reactions have been shown to be performed in a single operation, in the same reaction apparatus, and under same reaction conditions.^{10–13} Cascade synthesis has been reported to be more economic and environmentally friendly since it requires less solvents, reagents, energy and labour and can reduce waste discharge.^{6–13} Recent years have witnessed the exciting advancements of cascade reactions for the efficient preparation of natural products, pharmaceuticals and agrochemicals.^{6–13} However, cascade synthesis for organic functional dyes has been rarely reported.

Recent studies have shown that pyrylium salts constitute a unique class of organic functional dyes that can be used as photoredox catalysts, molecular probes, ionic liquids and optical sensors.^{14–26} Pyrylium salts have been shown to serve as strong excited state oxidants and they produce neither singlet oxygen nor superoxide radical anions during electron-transfer photooxygenation.^{14–18,22,23} Unlike conventional amine-reactive fluorescent probes, pyrylium salts have been reported to convert to pyridinium compounds after protein labelling, leading to drastic changes of the spectroscopic and luminescence properties.^{19–21} For the synthesis of pyrylium salts,^{18,24–28} the condensation reaction has been mostly selected where aromatic ketones, aldehydes and strong acids were used to afford pyrylium yields of 10–40%. HClO₄ has been frequently used to catalyse the condensation of benzaldehyde and acetophenone to form 2,4,6-triphenylpyrylium perchlorate which is strongly emissive and can be used as the photoredox catalyst. However, concentrated HClO₄ and even the pyrylium perchlorate in the dry form are explosive.^{18,29} It is of practical importance to develop efficient methods that can convert simple substrate into pyrylium salts under mild conditions and with higher yields.

Here we report efficient cascade reactions for the synthesis of pyrylium salts from simple aromatic substrates and acetic anhydride catalysed by light rare-earth metal triflates (Fig. 1a). Light rare-earth elements are earth-abundant and their triflates are cheap. The pyrylium yields of the cascade reactions can reach 50% by optimizing the reaction conditions and increasing the concentration of catalysts. The cascade reactions have been found to be further coupled to supramolecular assembly in aqueous medium to produce luminescent pyrylium nanoparticles that can be used for protein labelling.

Results and discussion

A homogeneous colourless solution of anisole, acetic anhydride and europium(III) triflate was heated to give a dark brown reaction mixture (Fig. 1b and Fig. S1, ESI†). Thin-layer chromatography (TLC) using dichloromethane as the mobile phase shows a yellow product that possesses a very small R_f value and exhibits



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Fig. 1 (a) Schematic illustration of the cascade synthesis of 730. (b) Photographs of the dark brown reaction mixture after the cascade reaction. (c) Thin-layer chromatography of the reaction mixture exhibiting the formation of a bright greenish yellow luminescent compound under 365 nm UV lamp. "*S*", "*X*" and "*R*" represent the starting substrate (anisole), the combination of the starting substrate and the reaction mixture, and the reaction mixture, respectively. (d) UV-Vis and steady-state emission spectra of 730 solutions in dichloromethane. (e) Single-crystal structures of 730.

bright greenish yellow emission under 365 nm UV lamp (Fig. 1c and Fig. S2, ESI[†]). The product can be purified by column chromatography or recrystallization in acetonitrile/diethyl ether. The product is found to be soluble in dichloromethane, chloroform, acetone, acetonitrile and dimethyl sulfoxide, but not soluble in *n*-hexane, diethyl ether and methanol. A dilute solution of the product in dichloromethane displays intense absorption band at 449 nm in its UV-vis spectrum (Fig. 1d). Upon excitation at 384 nm, the dilute solution of the product in dichloromethane exhibits emission band in the range of 450 nm to 600 nm with emission maxima at 498 nm (Fig. 1d). The photoluminescence quantum yield has been determined to be 90.7%. The product was further characterized by ¹H NMR, ¹³C{¹H} NMR, ¹⁹F NMR, LRMS, HRMS, FT-IR, melting point measurement, and single crystal X-ray diffraction (Fig. 1e and Fig. S3-S7, ESI[†]). These structural and photophysical studies indicate that the cascade reaction of anisole, acetic anhydride and europium(III) triflate can produce 2,4-bis (4-methoxyphenyl)-6-methylpyrylium triflate, 730. In control experiment, no. 730 was formed by heating the mixture of anisole and acetic anhydride in the absence of europium(m) triflate (Fig. S8, ESI[†]).

As summarized in Table 1, the reaction conditions were optimized by adjusting the feed ratios, catalyst concentration, reaction time and temperature. A reaction yield of 23.1% can be achieved with 5 equimolar quantities of acetic anhydride and 10 mol% europium(m) triflate catalyst at 135 °C after 6 h reaction; acetic anhydride serves as reagents and solvents. Samarium(m) triflate and lanthanum(m) triflate can also catalyse the reaction but are less efficient. The light rare-earth elements serve as a Lewis acid to catalyse the cascade reaction in the present study. With reference to the reported studies, europium(m) possesses slightly stronger Lewis acidity than

Table 1 Cascade synthesis of 730 at different reaction conditions

$0.92 \text{ mmol} x \text{ equiv} y \text{ equiv. } M(OTf)_3 \rightarrow O \qquad O$						O O O Tf
Entry	x (equiv.)	y (equiv.)	М	z (hour)	$T(^{\circ}C)$	$\operatorname{Yield}^{b}(\%)$
1	1	0.1	Eu	1.25	135	3.9
2	2	0.1	Eu	1.25	135	12.1
3	5	0.1	Eu	1.25	135	13.2
4	10	0.1	Eu	1.25	135	7.0
5	5	0.1	Eu	2	135	14.3
6	5	0.1	Eu	4	135	18.4
7	5	0.1	Eu	6	135	23.1
8	5	0.1	Eu	8	135	20.9
9	5	0.1	Sm	6	135	21.0
10	5	0.1	La	6	135	13.4
11	5	0.1	Eu	6	75	7.2
12	5	0.1	Eu	6	200^a	15.5
13	5	0.01	Eu	6	135	3.2
14	5	0.05	Eu	6	135	11.9
15	5	0.2	Eu	6	135	33.2
16	5	0.5	Eu	6	135	44.6
17	5	0.6	Eu	6	135	52.5
18	5	0.8	Eu	6	135	48.1
19	5	0.9	Eu	6	135	44.8

^{*a*} Reflux. ^{*b*} The reaction mixture was first diluted by acetonitrile and then the yield was determined by UV-vis measurements monitored at 425 nm.

samarium(m), and both europium(m) and samarium(m) have much stronger Lewis acidity than lanthanum(III).³⁰ These can explain the fact that europium(III) triflate is a more effective as catalyst for the synthesis of 730, than is either samarium(III) or lanthanum(III). The use of solvents such as dichloromethane, diethyl ether and acetonitrile and the presence of triethylamine have been found to quench the reaction. Light rare-earth elements that are earth-abundant and their triflates are much cheaper than heavy rare-earth elements. By increasing the concentration of europium(III) triflate, the reaction yield has been found to reach 52.5% as shown in entry 17 (Table 1). In the literature, most methods for pyrylium synthesis based on the condensation reactions of aromatic ketones or aldehydes using strong acids as catalysts have been reported to also afford high reaction yields. It is noteworthy that pyrylium synthesis from simple aromatic substrates that is cost-effective and straightforward with such a decent yield remains rarely reported. This cascade synthesis can be extended to other substrates such as 3',4',5'-trimethoxyacetophenone (Experimental section).

To investigate the reaction pathway of the cascade synthesis, the reaction of 4-methoxyacetophenone, acetic anhydride and europium(m) triflate was performed. It is found that the reaction can lead to 730 with a yield of 32.7%. Control experiment of the reaction of 4-methoxyacetophenone and acetic anhydride shows that no 730 formed in the absence of europium(m) triflate catalyst. In the reaction mixture of anisole, acetic anhydride and europium(m) triflate, the formation of 4-methoxyacetophenone was evidenced by TLC (Fig. S9, ESI⁺) and also supported by the reported studies.³¹ These indicate that the first step of the cascade reaction is Friedel–Crafts acylation of anisole catalysed



Scheme 1 (a) Formation of 730 from the reaction of 4-methoxy-acetophenone, acetic anhydride and europium(III) triflate. (b) Formation of 730 from the reaction of 4,4'-dimethoxy- β -methylchalcon, acetic anhydride and europium(III) triflate. (c) Proposed mechanism of the cascade reaction pathways for the synthesis of 730.

by europium(III) triflate to form 4-methoxyacetophenone (Scheme 1a). In addition, the reaction of 4,4'-dimethoxy- β -methylchalcon (the product from Aldol condensation of 4-methoxyacetophenone) and acetic anhydride catalysed by europium(III) triflate can produce 730 with a yield of 56.3% (Scheme 1b). No reaction occurs in the mixture of 4,4'-dimethoxy-βmethylchalcon and acetic anhydride without the addition of europium(III) catalyst. As Lewis acids, lanthanide(III) triflates have been reported to catalyse Aldol condensation.³² However, TLC of the reaction mixture of anisole, acetic anhydride and europium(III) triflate shows the absence of 4,4'-dimethoxy-βmethylchalcon (Fig. S9, ESI†). These experiments suggest two possible reaction pathways of the europium(III) catalytic conversion of 4-methoxyacetophenone and acetic anhydride to form 730 as shown in Scheme 1c. Possible pathway (1): europium(m)-catalysed Aldol condensation of 4-methoxyacetophenone into 4,4'-dimethoxy-\beta-methylchalcon, followed by the formation of unsaturated 1,5-diketone intermediates and finally the fast formation of 730.^{18,33} In possible pathway (2) of a threecomponent reaction, europium(III) organizes two 4-methoxyacetophenone to form unsaturated 1,5-diketone intermediates which can fast convert into 730. Light rare-earth catalysts are indispensable for the chemical transformation of all the reaction steps. Compared to the conventional methods for pyrylium synthesis where aromatic ketones, aldehydes and strong acids are used, the present cascade catalysis is mild, efficient and cheap.

The cascade reaction mixture can also be purified by recrystallization in deionized water (Fig. S10, ESI⁺). Addition of deionized water to a dilute 730 solution is found to form pyrylium aqueous suspension that exhibits the Tyndall effect (Fig. 2a and 3b). Dynamic light-scattering (DLS) analysis of the aqueous suspension gave an average hydrodynamic diameter of 67.3 nm and a polydispersity index of 0.167 (Fig. 2b). Transmission electron microscopy (TEM) observations showed the formation of spherical nanoparticles with a diameter of 49.7 \pm 8.6 nm (Fig. 2c and d). The TEM results agree with DLS studies since 730NPs that consist of 730 molecules and a certain amount of water drying at ambient conditions can undergo shrinkage during TEM sample preparation and DLS results are sensitive to nanoparticles with larger sizes. The zeta-potential of the aqueous suspension was measured to be +46.9 mV (Fig. S12, ESI⁺). In view of the amphiphilic nature of 730 pyrylium salts, it is proposed that the spherical pyrylium nanoparticles in the aqueous medium are formed by supramolecular assembly of 730 molecules driven by the aggregation of the hydrophobic 4-methoxyphenyl groups and stabilized by the positively charged pyrylium groups.

The aqueous pyrylium nanoparticles are found to be stable after long-term storage under ambient conditions (Fig. S13, ESI[†]). The 730NPs in aqueous medium were tested for protein labelling (Fig. 3a). Upon mixing the aqueous 730NPs with bovine serum albumin (BSA) aqueous solution followed by 1 hour room-temperature incubation, the luminescence colour of pyrylium nanoparticles changed from yellow to blue (Fig. 3b). After passing through a Sephadex G-10 column to remove free 730, the purified BSA-730 conjugates show absorption band in the range of 300 nm to 400 nm with maxima at 337 nm (blue curve in Fig. 3c), which suggest the formation of pyridinium groups by the reaction of pyrylium groups with primary amine groups on BSA (Fig. 3a).¹⁹ The disappearance of absorption signals in the range of 400 nm to 500 nm indicates unconjugated 730 have been completely removed by Sephadex G-10 column filtration (Fig. 3c). Upon excitation, the purified BSA-730 conjugates exhibit emission band in the range of 350 nm to



Fig. 2 (a) Schematic illustration of the preparation of 730NPs by supramolecular assembly. (b) The distribution of hydrodynamic diameters of 730NPs obtained by DLS studies. (c) TEM images and (d) the corresponding size distribution of 730NPs.



Fig. 3 (a) Schematic illustration of protein labelling by aqueous pyrylium. (b) Photographs of BSA aqueous solution, crude BSA-730 conjugates, 730NPs, free 730 in Sephadex G-10 column and purified BSA-730 conjugates under 365 nm UV lamp. (c) UV-Vis spectra of BSA, 730NPs and BSA-730 conjugates. The arrow indicates the absorption band of pyridinium groups in the range of 300 nm to 400 nm. (d) Steady-state emission spectra of 730NPs (excited at 384 nm) and BSA-730 conjugates (excited at 337 nm).

550 nm with emission maxima at 427 nm (Fig. 3d), which can be attributed to the formation of pyridinium functional groups. The purified BSA-730 conjugates are found to possess long-term stability (Fig. S14, ESI⁺). It is noteworthy that, before BSA labelling, the aqueous pyrylium nanoparticles show absorption band at 421 nm in the UV-vis spectra and exhibit emission band at 516 nm upon excitation (Fig. 3c and d). When compared to the amine-reactive organic dyes such as Alexa Fluor[®] series,³⁴ a distinct feature of the pyrylium dye for protein labelling is the drastic spectroscopic and luminescence change before and after labelling, which allows direct monitoring of the labelling reaction by the naked eye. Another interesting feature of protein labelling by the aqueous pyrylium nanoparticles is the minimum contact between organic solvent and proteins during the mixing of protein and pyrylium; the standard protocol of Alexa Fluo[®] dye labelling includes the direct mixing of dye solution in DMSO or DMF with protein solution, which may cause denaturation of labile proteins. Last but not least, the pyrylium dyes are much cheaper than conventional amine-reactive dyes such as Alexa Fluor[®] series.

Conclusions

In conclusion, efficient cascade reactions for the synthesis of pyrylium salts from simple aromatic substrates and acetic anhydride have been developed to achieve pyrylium yields as high as 52.5% under mild conditions. Catalysed by light rareearth metal triflates, the cascade synthesis has been found to proceed by two possible reaction pathways: (1) from Friedel-Crafts acylation through Aldol condensation to fast pyrylium formation; (2) Friedel-Crafts acylation followed by threecomponent reaction of pyrylium formation. The cascade reactions have been found to be further coupled to supramolecular assembly to produce luminescent pyrylium nanoparticles in aqueous medium that can function as protein biolabels. Given that the light rare-earth elements are cheap and earth-abundant, further studies would be placed at the development of other value-added chemical transformation catalysed by light rare-earth elements, as well as the applications of the obtained organic functional molecules.

Experimental

Physical measurements and instrumentation

¹H NMR (400 MHz), ¹³C{¹H} NMR (100 MHz) and ¹⁹F NMR (376 MHz) spectra were recorded on a JEOL Fourier-transform NMR spectrometer (400 MHz). Mass spectra were performed on Agilent Technologies 5973N and Thermo Fisher Scientific LTO FT Ultra mass spectrometer. FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a resolution of 4 cm⁻¹. Differential scanning calorimetry (DSC) was performed on a TA Q200 DSC instrument in nitrogen with a heating rate of 20 °C min⁻¹. Single-crystal X-ray diffraction analysis was performed on a D8 VENTURE SC-XRD instrument. The X-ray crystallographic data for 730 has been deposited at the (CCDC[†]), under the deposition number CCDC[†] 2054845. UV-Vis absorption spectra were recorded on a Techcomp UV1050 UV-vis spectrophotometer. Emission spectra were recorded using Hitachi FL-7000 fluorescence spectrometer. Zeta-potential analysis and dynamic light scattering (DLS) experiments were performed on a Malvern Nano-ZS90 Zetasizer with an internal HeNe laser (λ = 632.8 nm). Transmission electron microscopy (TEM) experiments were performed on a FEI Talos F200S transmission electron microscope with an accelerating voltage of 120 kV. TEM samples were prepared by depositing a drop of sample solution onto a carbon-coated copper grid followed by drying under ambient conditions. The sizes of the nanoparticles were analyzed using ImageJ 1.53c software.

Synthesis of 2,4-bis(4-methoxyphenyl)-6-methylpyrylium triflate (730) *via* cascade reaction

Into a round bottom flask were added anisole (0.100 mL, 0.92 mmol), acetic anhydride (0.435 mL, 4.60 mmol) and europium(m) triflate (55.1 mg, 0.092 mmol). The reaction mixture was heated to 135 °C and stirred for 6 h. After cooling to room temperature, the reaction mixture was poured into an excess of diethyl ether (20 mL) to form 730 precipitates. The precipitates were filtered and washed with diethyl ether, then recrystallized twice by acetic acid and diethyl ether. The obtained red crystals was washed with diethyl ether and dried under vacuum. 730 can also be purified by recrystallization in acetonitrile/deionized water. Both acetic anhydride/diethyl ether and deionized water can dissolve europium(m) triflates, so the recrystallization process can remove europium triflate. Single crystal of 730 was obtained by slow vapour diffusion of diethyl ether into an acetonitrile solution of 730 or a 730 reaction

mixture. Melting point of 730 was measured by DSC to be 274 °C. ¹H NMR (400 MHz, 298 K, DMSO- d_6 , relative to Me₄Si/ppm) δ 8.87 (s, 1H), 8.51-8.42 (m, 4H), 8.40 (s, 1H), 7.33-7.23 (m, 4H), 3.97 (s, 3H), 3.95 (s, 3H), 2.89 (s, 3H). ¹³C¹₁H} NMR (100 MHz, 298K, DMSO-*d*₆) δ 174.12, 169.91, 165.43, 164.69, 162.50, 132.28, 130.74, 123.94, 122.20, 121.20, 118.99, 115.55, 115.26, 115.05, 111.38, 56.09, 55.99, 20.75. CF₃ group of triflate should possess quartet signal due to CF coupling. The present ¹³C¹H NMR spectrum only shows two peaks of CF3 group at 118.99 and 122.20 ppm because of relatively low sample concentration and relatively short data collection time. ¹⁹F NMR (376 MHz, 298 K, DMSO- d_6 , relative to CFCl₃/ppm) δ -78.03. FT-IR (KBr, cm⁻¹): 3080, 2942, 2846, 1643, 1593, 1533, 1505, 1477, 1460, 1441, 1407, 1356, 1305, 1260, 1223, 1180, 1157, 1030, 947, 839, 637, 571, 550, 517. LRMS, m/z 307.1. HRMS m/z found (calcd for C₂₀H₁₉O₃): 307.1328 (307.1329).

Synthesis of 2-methyl-4,6-bis(3,4,5-trimethoxyphenyl) pyrylium triflate (345) *via* cascade reaction

Into a round bottom flask were added 3',4',5'-trimethoxyacetophenone (0.193 mg, 0.92 mmol), acetic anhydride (0.435 mL, 4.60 mmol) and europium(III) triflate (55.1 mg, 0.092 mmol). The reaction mixture was stirred for 2 days. After cooling to room temperature, the reaction mixture was poured into an excess of diethyl ether (20 mL) to form precipitates. The precipitates were filtered and washed with diethyl ether, and then recrystallized twice with acetic acid and diethyl ether. The obtained brown crystals were washed with diethyl ether and dried under a vacuum. ¹H NMR (400 MHz, 298 K, DMSO-d₆, relative to Me₄Si/ppm) δ 8.93 (d, *J* = 1.8 Hz, 1H), 8.57 (d, *J* = 1.8 Hz, 1H), 7.69 (s, 2H), 7.65 (s, 2H), 3.99 (s, 6H), 3.98 (s, 6H), 3.87 (s, 3H), 3.86 (s, 3H). LRMS, *m*/*z* 427.2. HRMS *m*/*z* found (calcd for C₂₄H₂₇O₇): 427.1751 (427.1749).

Synthesis of 4,4'-dimethoxy- β -methylchalcon

To a stirred mixture of the 4-methoxyacetophonone (150.2 mg, 1.00 mmol) and anhydrous ethanol (0.295 mL, 5.00 mmol), thionyl chloride (0.121 mL, 1.67 mmol) was added.³⁵ When the solution turned deep red, saturated NaHCO₃ was added and the mixture was extracted twice with dichloromethane (20 mL). The organic layer was separated and dried over anhydrous Na₂SO₄. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane as the eluent to give 4,4′- dimethoxy-β-methylchalcon with a yield of 62%.

Conflicts of interest

There are no conflicts to declare.

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