



## Rational design of slightly twisted coumarin molecules with remarkable solution and solid dual efficient luminescence



Yue Sun<sup>b</sup>, Tong Wu<sup>a, b</sup>, Fang Zhang<sup>a</sup>, Rong Zhang<sup>a</sup>, Min Wu<sup>a</sup>, Yuezhen Wu<sup>a</sup>, Xiaozhong Liang<sup>a</sup>, Kunpeng Guo<sup>a, \*</sup>, Jie Li<sup>a, \*\*</sup>

<sup>a</sup> Ministry of Education Key Laboratory of Interface Science and Engineering in Advanced Materials, Research Center of Advanced Materials Science and Technology, Taiyuan University of Technology, Taiyuan, 030024, China

<sup>b</sup> School of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

### ARTICLE INFO

#### Article history:

Received 28 July 2017

Received in revised form

18 September 2017

Accepted 25 September 2017

Available online 27 September 2017

#### Keywords:

Coumarin derivatives

Slightly twisted conformation

Intramolecular charge transfer

Molecular packing pattern

Dual efficient luminescence

### ABSTRACT

Endowing slightly twisted molecules highly emissive in both solution and solid state is of great importance for understanding the principle of maximizing the luminescent efficiency of luminophores. To this end, a series of slightly twisted coumarin luminophores **CMs** with different alkoxy substituents at the 7-positions were synthesized. The effect of the substituents on the diversity photophysical properties of the four compounds in solution, THF/H<sub>2</sub>O mixtures and solid state were investigated. Comparing to the referenced compound **CM** (3-*p*-tolyl-2H-chromen-2-one) that without a substitute, the introduced electron-rich alkoxy substituents not only enhanced the intramolecular charge transfer (ICT) effect, but also significantly modified their molecular packing patterns in the crystals. The combined effect of increasing the radiative and suppressing the nonradiative pathways boosted the luminescence efficiency of **CM1–CM3** in solution and the solid state simultaneously. Eventually, compound **CM2** with an ethoxy substituent exhibited the strongest blue emission with fluorescence quantum yields as high as 73.2% and 96.7% in solution and the solid state, respectively. This work presents an efficient strategy towards dual strong fluorescent luminophores in both solution and the solid state.

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### 1. Introduction

Highly emissive organic materials have attracted great attention due to their applicability in the fields of optoelectronic devices, chemosensors and bioprobes [1–18]. Although the emission of a number of traditional organic luminophores is efficient in dilute solution, it tends to decrease or even quench in the aggregated or solid states [19–22]. This aggregation-caused quenching (ACQ), which mainly caused by internal conversion, intersystem crossing, intermolecular electron transfer, as well as excimer or exciplex formation and isomerization, significantly limits the organic luminophores for their practical applications [23]. To prevent or alleviate these nonradiative pathways, numerous endeavors through molecular engineering and physical technology have been made, including the introduction of bulky substituents, enhanced intramolecular charge transfer (ICT) transition, cross-dipole

packing and aggregated formation [24–34]. In 2001, Tang's group reported a series of silole derivatives with propeller-like conformations that was nonemissive in dilute solutions, but highly luminescent when aggregated into solid state [35]. Their work has attracted huge attention as an effective methodology to overcome ACQ, and this novel phenomenon was termed as aggregation-induced emission (AIE). Since then, various AIE materials with efficient luminescence in the solid state have been prepared for diverse applications [36–40].

To realize intense luminescence in the solid state, most AIE molecules adopt highly twisted conformations to restrict intramolecular rotation (RIR) or adverse intermolecular interactions [41–47]. However, such molecules often emit weak emission in solution, which limits their wide range of applications. Studies of developing molecules possess intense luminescence in both solution and the solid state have, to the best of our knowledge, been focused on restricting free rotation of a single bond in twisted AIE molecules through conjugation-induced rigidity or increasing steric hindrance [48–50]. However, the exploration of dual efficient luminescent materials based on slightly twisted molecules is still

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [guokunpeng@tyut.edu.cn](mailto:guokunpeng@tyut.edu.cn) (K. Guo), [lijie01@tyut.edu.cn](mailto:lijie01@tyut.edu.cn) (J. Li).

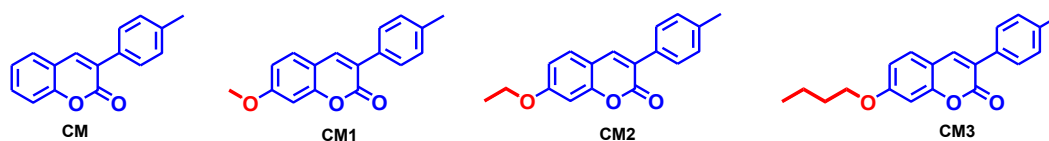
challenging. This is probably arisen from the difficulties of luminescence optimization from molecular level to molecular packing pattern control in solution and the solid state.

Coumarin (chromen-2-one) derivatives have been widely studied and become a class of fluorescent dyes of intense interest due to their promising applications in organic lasers, organic light-emitting diodes and fluorescent sensors [51–59]. It is well known coumarin derivatives give intense emission in solution, but poor luminescence in the aggregated and solid state because their planar skeletons are prone to form strong  $\pi$ - $\pi$  stacking [60]. To expand their real-world utilization, an AIE coumarin derivative based on the RIR mechanism has been designed and synthesized [61]. However, the reported AIE coumarin derivative still emits weakly in its solution. Thus, the exploration of facile ways to obtain dual efficient fluorescent coumarin derivatives, especially those with slightly twisted conformations, is of high importance for structure-property understanding and practical applications. Herein, we developed four coumarin derivatives (Scheme 1) and investigated their photophysical properties systematically. Comparing with the referenced compound **CM** (3-*p*-tolyl-2H-chromen-2-one), its alkoxy substituted derivatives at the 7-positions **CM1**–**CM3** showed boosted luminescence in both solution and the solid state due to the synergistic effect of the ICT characteristic and the molecular packing modification by the alkoxy tail. Among them, **CM2** with an ethoxyl substitute exhibited the strongest blue emission with absolute fluorescence quantum yields ( $\Phi_{FS}$ ) of 73.2% and 96.7% in THF solution and the solid state, respectively.

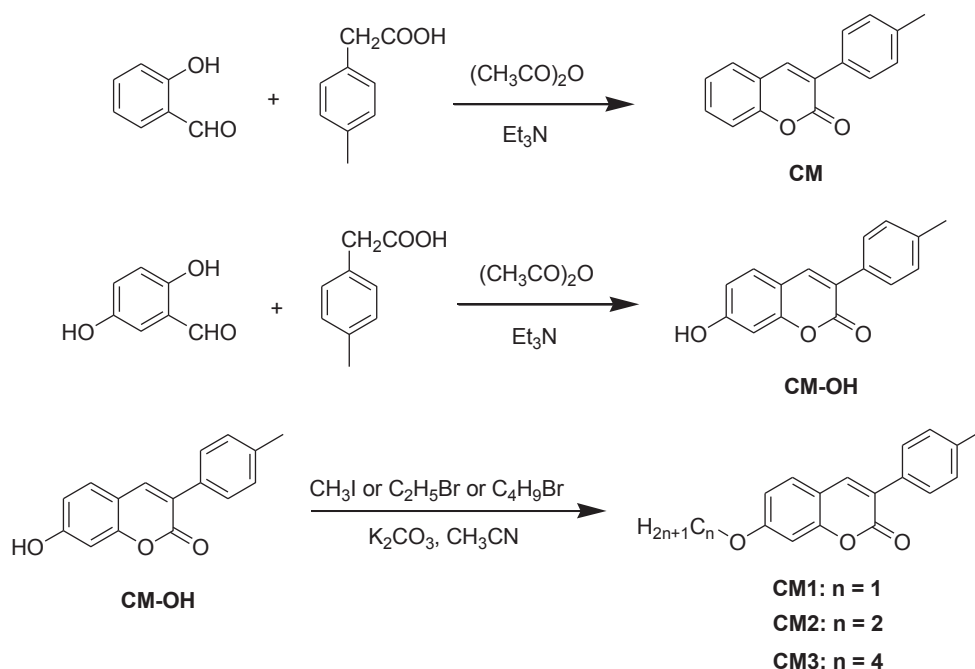
## 2. Experimental section

### 2.1. Materials and characterization

All chemicals for synthesis were purchased from Energy Chemical and used without purification. Reactions were monitored by TLC silica plate (60F-254). NMR spectra measurements were carried out at Bruker 600 MHz for  $^1\text{H}$  NMR and 151 MHz for  $^{13}\text{C}$  NMR, using chloroform- $d$  as the solvent. Chemical shifts were reported in parts per million (ppm) relative to internal TMS (0 ppm). Splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m). Mass spectra were measured on Microflex MALDI-TOF mass spectrometer. UV-Vis spectra were recorded in a HITIACH U-3900 spectrometer. Photoluminescent (PL) spectra were recorded in a HORIBA FluoroMax-4 spectrometer. The absolute fluorescence quantum yields ( $\Phi_F$ ) of solutions (10  $\mu\text{M}$ ) and powders were measured on HORIBA FluoroMax-4 by using a calibrated integrating sphere. The quartz cuvettes used were of 1 cm path length. Powder X-ray diffraction (XRD) of the samples was characterized using a Philips high resolution X-ray diffraction system (model PW1825). X-ray single-crystal diffractions of **CM** and **CM2** were performed on a Bruker SMART APEX II diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71000 \text{ \AA}$ ). The structures were solved with direct method (SHELX-97) and refined with full-matrix least-squares technique. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically placed. Relevant crystal collection data, refinement data for the crystal structures



Scheme 1. Molecular structures of **CM**, **CM1**, **CM2** and **CM3**.



Scheme 2. The synthetic route for compounds **CM**, **CM1**, **CM2** and **CM3**.

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