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Research paper

Design and chiroptical properties of a water-soluble and violet-blue emissive alkyne template

Tingchao He[a,b,1], Yi Zhang[a,1], Song Yao[a], Xingrong Li[a], Fenghuan Zhao[c], Xiaodong Lin[a], Jiuxu Xia[d], Wei Lu[d], Chuanxiang Ye[a], Rui Chen[c,*], Junmin Zhang[a,*]

[a] College of Physics and Energy & College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, China
[b] Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, Shenzhen University, Shenzhen 518060, China
[c] Department of Electrical and Electronic Engineering, South University of Science and Technology of China, Shenzhen 518055, China
[d] Department of Chemistry, South University of Science and Technology of China, Shenzhen 518055, China

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ABSTRACT

Circular dichroism (CD) and circular polarized luminescence (CPL) are useful for various applications. However, it is difficult to achieve excellent CD and CPL in differently polar solvents simultaneously. This work provides a simple but efficient way to construct violet-blue fluorescent and water-soluble chromophore through the construction of rigid conformation of the alkyne architecture. By introducing proline pendants into alkyne architecture, the chromophore exhibits reasonable CD and CPL properties in the lowly and highly polar solvents. More importantly, even in water, the chromophore displays effective CD anisotropy factor ($g_{abs} \sim 1 \times 10^{-3}$) and luminescence dissymmetry factor ($g_{lum} \sim 2 \times 10^{-3}$), as well as high fluorescence quantum yield (Φ up to 35%). Additionally, the chromophore exhibits large two-photon CD according to the theoretically calculated results. The excellent chiroptical properties from the simple organic fluorophore enables its future applications in miniatured optoelectronic devices and CPL-based bioimaging.

1. Introduction

Recently, chiroptical phenomena, including circular dichroism (CD) and circularly polarized luminescence (CPL), have received growing interest due to the development of smart photonic materials for advanced technologies [1–9]. CD measurements are used to reveal the chirality of ground state molecules, while applications of CPL have primarily been used to obtain structural information about molecular excited states [10]. More importantly, there has been a growing interest in developing optical materials that are capable of emitting CPL because of their potential applications in information storage and processing, 3D displays, spintronics-based devices, biological probes and signatures, security tags, CPL lasers, enantioselective CPL sensors and CPL microscopes [1,2,11–14].

So far, there have been lots of reports on various CD and CPL materials, such as lanthanide complexes [15], conjugated polymers [16], metal nanoparticles [17], semiconductor quantum dots [18], simple organic molecules [19], and so on. Although there are numerous examples of optical materials that show reasonable chirality in organic solvents or solid state, previous literatures reported their chiral behaviors in only one or two media [20,21]. The influences of solvent polarity on CD and CPL of materials have been rarely explored. Even though there are occasional chiral materials investigated in different two solvents, they suffer from serious attenuation of chiroptical behaviors in highly polar media, especially in water [22]. It is not beneficial for extending their chiroptical applications.

From the viewpoint of applications, chiral optoelectronic devices are likely to be exposed to complicated environments, so the robust chirality of materials again environmental alteration, such as solvent polarity, should be extremely important. Therefore, there is an urgent requirement to develop simple molecules with reasonable or robust chirality in differently polar solvents. To the best of our knowledge, there are few chiral materials exhibiting reasonable CD and CPL dissymmetry factors ($> 1 \times 10^{-3}$) in different media ranging from lowly to highly polar solvents. Except aggregation induced chiral molecular self-assembled structures [23,24], scarce organic simple molecules shows effective luminescence quantum yield (QY, $\Phi > 30\%$) in water. The development of such kinds of simple molecules is of great importance, since they would be active chiral materials for various potential applications. Therefore, research guidelines directed toward the

* Corresponding authors.
E-mail addresses: chen.r@sustc.edu.cn (R. Chen), zhangjm@szu.edu.cn (J. Zhang).
[1] Equal contributions.

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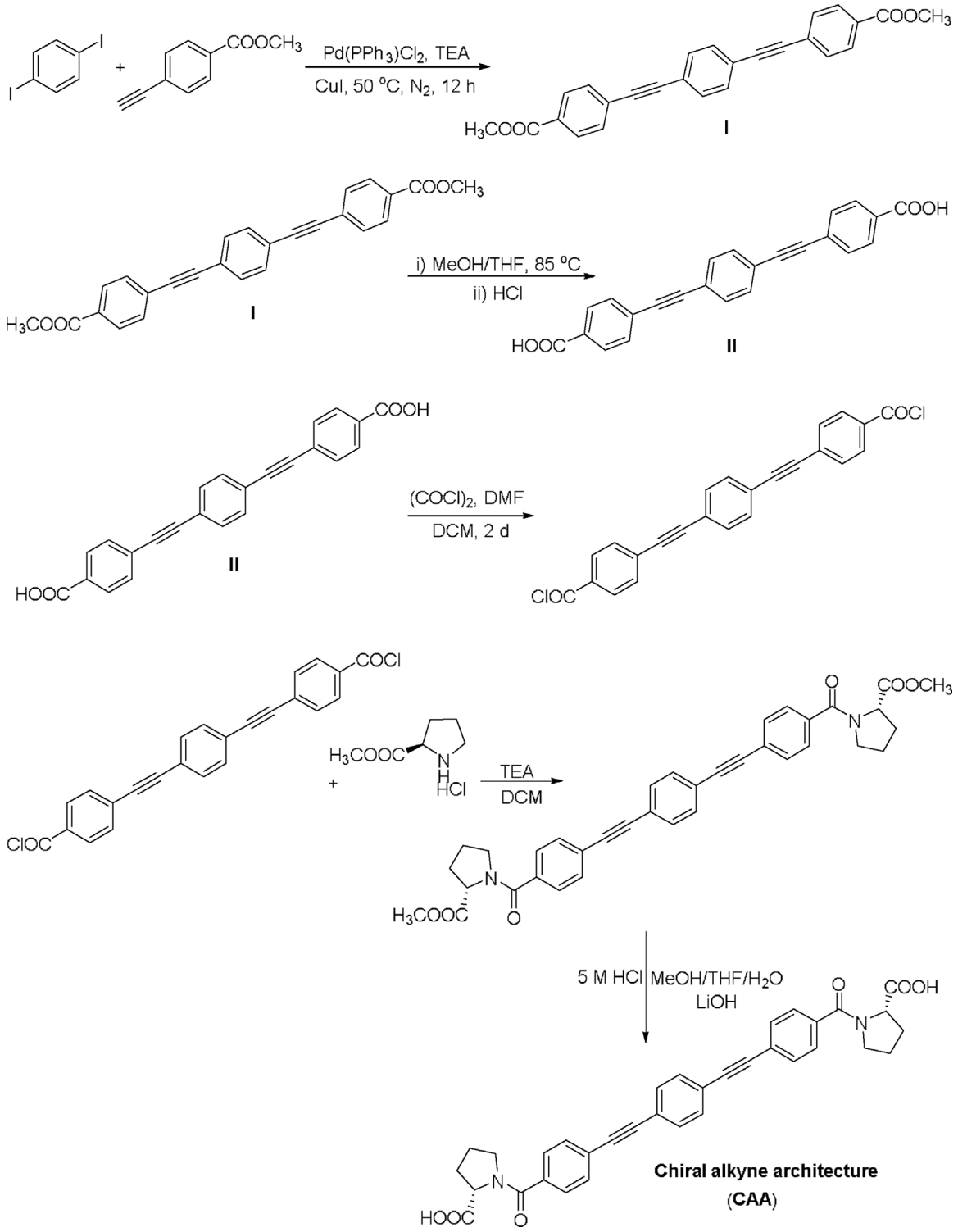

Scheme 1. The synthesis protocol of the chiral alkyne architecture (4,4′-(1,4-phenylenebis(ethyne-2,1-diyl))bis(benzoyl))diproline).

expansion of organic molecules enabling excellent CD and CPL in various organic solvents are urgently needed.

In this work, we report the design and synthesis of one novel chiral alkyne architecture, which is covalently tethered by two identical chiral proline pendants. Interestingly, the chromophore shows efficient CD and CPL behaviors in differently polar solvents. Especially, no obvious attenuation of CPL properties has been observed in water, which we believe should have a broad range of potential applications. Additionally, the theoretically calculated results indicate the chromophore exhibits large two-photon CD (TP-CD), which is defined as the difference between two-photon absorption (TPA) for left and right circular polarization light, respectively. Therefore, the chromophore is a useful TP-CD probe and has unique fingerprinting functionality for chiral species.