



A new organic far-red mechanofluorochromic compound derived from cyano-substituted diarylethene

Xiqi Zhang^{a,*}, Zhiyong Ma^b, Meiyong Liu^c, Xiaoyong Zhang^a, Xinru Jia^b, Yen Wei^{a,*}

^a Department of Chemistry and the Tsinghua Center for Frontier Polymer Research, Tsinghua University, Beijing 100084, China

^b Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

^c Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Organic Solids, Laboratory of New Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

A new cyano-substituted diarylethene derivative (**R-NH₂**) with reversible far-red mechanofluorochromic property was synthesized and confirmed by standard spectroscopic methods. To the best of our knowledge, the 684 nm red-shifted wavelength of the ground **R-NH₂** is the longest wavelength that has appeared in the literature. The mechanofluorochromic mechanism was investigated by small and wide-angle X-ray scattering and was ascribed to the destruction of crystalline structure. More in-depth study by infrared spectra and time-resolved emission-decay behaviors showed that the changes of C–H out-of-plane bending vibrations in aryl group of the compound and the obvious increase of fluorescence lifetime might be the fundamental reasons. The synthetic strategy reported here can be extended to prepare more and more long-wavelength emission mechanofluorochromic materials, which can broaden the scope of application of such materials and for thoroughly understanding the mechanofluorochromic mechanism.

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1. Introduction

Mechanofluorochromic materials have advanced fluorescent properties that change in response to external force stimuli and expected to generate new intelligent materials based on their superior high efficiency and reproducibility compared with conventional fluorescent materials, and have got wide applications in sensors, memory chips, and security inks.^{1,2} Chemical structure and molecular assembly structure changes are considered as two major mechanofluorochromic ways. Between them, molecular assembly structure change is believed easier to realize the dynamic control of fluorescent process. In 2002, Weder et al. reported on two cyano-substituted diphenylethene derivatives-doped linear low-density polyethylene as the first two mechanofluorochromic materials.³ Since then, the appeared organic mechanofluorochromic materials were still extremely rare until 2010 due to the lack of established property–structure relationship.^{4–8} In 2010, Xu et al. reported on a compound derived from tetraphenylethylene and divinylanthracene, which exhibited obvious mechanofluorochromic and aggregation-induced emission (AIE) properties.⁹ The

unique AIE materials have attracted great research interest because they could overcome the notorious issues in most planar conjugated organic dyes named aggregation-caused quenching (ACQ) effect. Different AIE architectural frameworks involving siloles, triphenylethene, tetraphenylethene, distyrylanthracene, cyano-substituted diarylethene derivatives conjugated molecules have been developed and utilized for chemosensor and bioimaging applications.^{10–30}

Since 2010, the Xu's group synthesized and reported a number of new mechanofluorochromic compounds with AIE feature,^{31–37} and proposed a 'molecular conformational planarization' mechanism for mechanofluorochromic compounds to establish a common structure–property relationship of the mechanofluorochromic materials and AIE materials, which would be helpful in identifying and synthesizing more novel mechanofluorochromic materials.¹ According to this relationship, a number of new organic mechanochromic fluorescent compounds were synthesized, which greatly broadened the field of mechanofluorochromic materials.^{38–56} In view of this situation, the very critical thing is either to discover new structures of mechanofluorochromic materials or to broaden the range of the fluorescent emission wavelength. Among the existing reported mechanofluorochromic materials, the fluorescent emission of them mainly located at short wavelength from blue to yellow due to their inherent conjugated groups. Rare

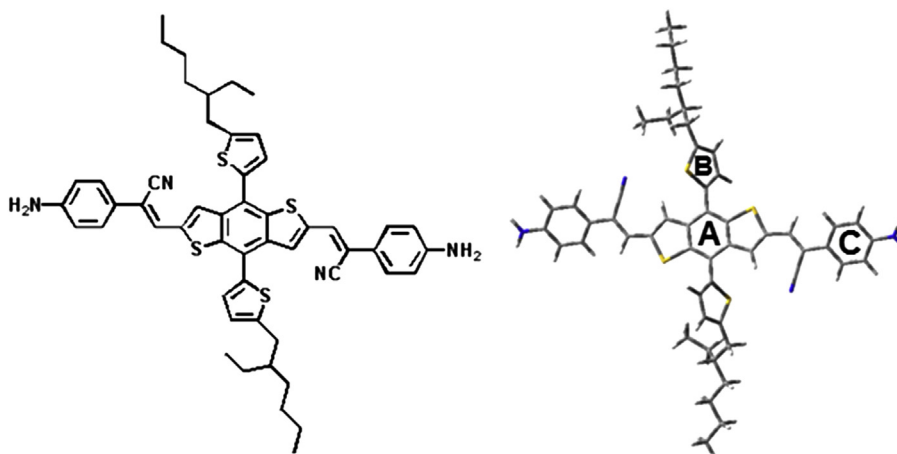
* Corresponding authors. E-mail addresses: sychezhang@126.com (X. Zhang), weiyen@tsinghua.edu.cn (Y. Wei).

mechanofluorochromic materials emit fluorescence with longer wavelength. Although Ooyama et al. reported on a dye **SO**₂ with red (625 nm) mechanofluorochromic property, only a 7 nm redshift was observed for the fluorescent emission wavelength after grinding the as-recrystallized dyes **SO**₂.⁵⁷

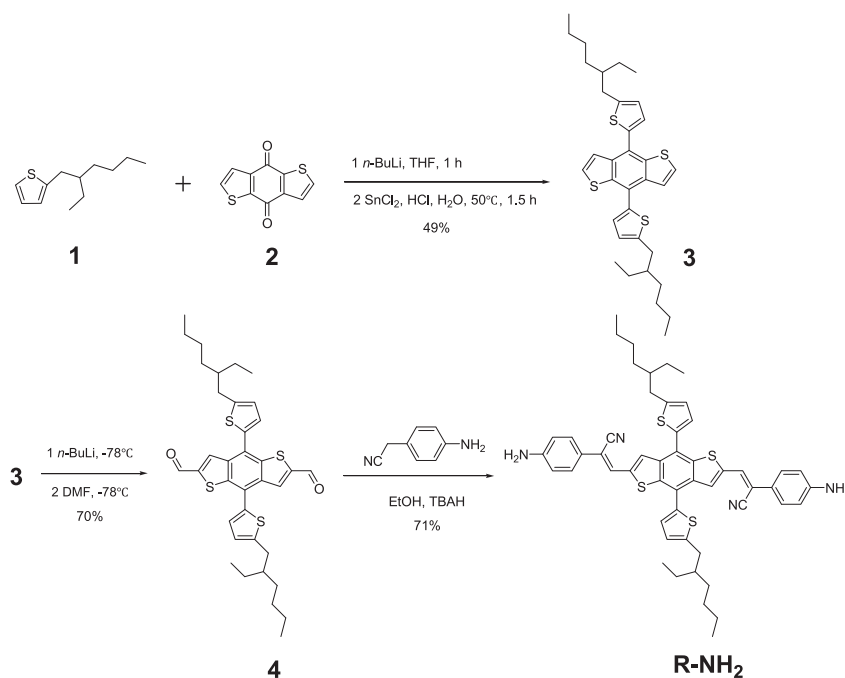
Herein, we report a new organic far-red fluorescent cyano-substituted diarylethene-based compound (**R-NH**₂) (derivatized from 4, 8-bis[5-(2-ethylhexyl)-2-thienyl]benzodithiophene core structure with bis[2-(4-aminophenyl)acrylonitrile] side chains) with reversible mechanofluorochromic property (Scheme 1). Solid-state fluorescent spectra and UV–vis spectra were studied to reveal the mechanofluorochromic property. Then, the mechanofluorochromic mechanism was investigated by differential scanning calorimetry (DSC), infrared spectra (IR), small and wide-angle X-ray scattering (SWAXS), and time-resolved emission-decay behaviors.

2. Results and discussion

The fluorogen **R-NH**₂ was prepared following the synthetic route shown in Scheme 2. Its structure was characterized and confirmed by standard spectroscopic methods. To gain the lowest energy spatial conformation of the compound, we conducted quantum mechanical computations by using the Gaussian 03 software.⁵⁸ The HOMO and LUMO of **R-NH**₂ were obtained (Fig. 1) according to the density functional method at the B3LYP/6-31 G level after the structural optimization. The HOMO of the compound showed dispersed electron cloud distributions on all of the aryl groups and amino groups on the molecule, whereas the electron cloud of the LUMO exhibited the migration from both ends of the amino and thienyl groups to aryl core and cyano groups. Moreover, the compound adopted a twisted spatial conformation, as shown in the optimized structure (Scheme 1, right). The dihedral angles of



Scheme 1. The chemical structure (left) and the optimization geometry (right) of **R-NH**₂.



Scheme 2. Synthetic route of **R-NH**₂.

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