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# A selective fluorescent and colorimetric probe for cyanide based on dual-site controlled intramolecular charge transfer–photoinduced electron transfer–Fluorescence resonance energy transfer

Hongwei Wu, Yayun Chen, Caihui Rao, Dongli Fan\*, Huazheng Wei, Chuanxiang Liu\*

School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 201418 Shanghai, PR China

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## ABSTRACT

A novel dual-site controlled intramolecular charge transfer–photoinduced electron transfer–Fluorescence resonance energy transfer (ICT–PET–FRET) probe **6b** and its reference ICT–FRET probe **6a** were designed and synthesized. The probes show high selective fluorescent and colorimetric sensing for cyanide ions. The NH and CH groups connected by the  $\pi$ -extension framework in probe **6b** were simultaneously employed as the two sensing sites and controlled the fluorescence of naphthalimide unites by PET, ICT followed by the corresponding FRET processes between coumarin and naphthalimide fluorophores.

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## Introduction

Anion recognition has received considerable attention for the important roles it plays in various chemical, biological, and environmental processes.<sup>1</sup> Among them, the cyanide ion ( $\text{CN}^-$ ) is highly toxic to humans and affects many normal functions in physiological systems,<sup>2</sup> such as the vascular, visual, central nervous, cardiac, endocrine, and metabolic systems.<sup>3</sup> Cyanide compounds are used in gold mining and electroplating industries and cause irreparable damage to the environment.<sup>4</sup> Thus, there is a great deal of interest in the development of selective, sensitive, and easy methods for  $\text{CN}^-$  detection. Optical sensors involving colorimetric and/or fluorescence changes for cyanide ion are of considerable interest because of their simple, inexpensive, and rapid implementation.<sup>5</sup> The conventional strategy for sensing cyanide uses the coordination ability and the nucleophilic reactivity of cyanide, which involve addition with metal-complexes, the displacement method, and the bond-forming reaction between the cyanide and either an electrophilic carbon or a boron center.<sup>6</sup> Although most of reported probes for cyanide are commonly concentrated on the mechanisms involving photo-induced electron transfer (PET) or intramolecular charge transfer (ICT), fluorescence probes for  $\text{CN}^-$  based on FRET are considerably limited.<sup>7</sup>

Fluorescence resonance energy transfer (FRET) has attracted much attention in the design of fluorescent probes for environmen-

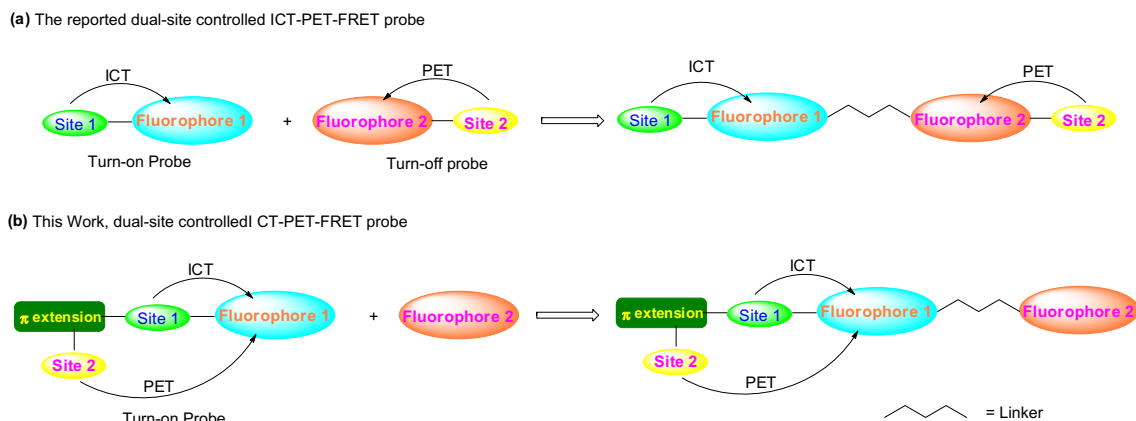
tal monitoring and medical diagnosis.<sup>8</sup> The popular strategies for designing FRET probes is to conjugate a fluorescent dye with a quencher (donor–quencher model), or to link two fluorescent dyes which can form the donor–acceptor pair (donor–acceptor model).<sup>9</sup> Recently, Lin's group reported a new strategy to construct a FRET platform using the coumarin–naphthalimide dyad, which involves changing the overlap level of the donor emission spectrum with the acceptor absorption via modulation of the acceptor fluorophore absorption wavelength to operate the FRET on/off process.<sup>10</sup> Lin's group also developed a novel ICT–PET–FRET fluorescent probe based on the dual-site for monitoring pH changes (Scheme 1, a).<sup>11</sup> While a variety of fluorescence and colorimetric probes for  $\text{CN}^-$  have been reported, to the best of our knowledge, little has been reported on fluorescence and colorimetric probes for  $\text{CN}^-$  based on dual-site controlled FRET.

In view of the above findings, and as part of our research effort devoted to anion recognition,<sup>12</sup> a further modification was made to a previous sensor containing the CHCN group by introducing the FRET process. A strategy involving the connection of the dual sites by the  $\pi$ -extension framework to construct the novel dual-site controlled ICT–PET–FRET model (Scheme 1, b) was developed for the first time.

## Results and discussion

The target compound **6a** and **6b** were synthesized in three steps as shown in Scheme 2. Intermediate **3** was synthesized by the

\* Corresponding authors.



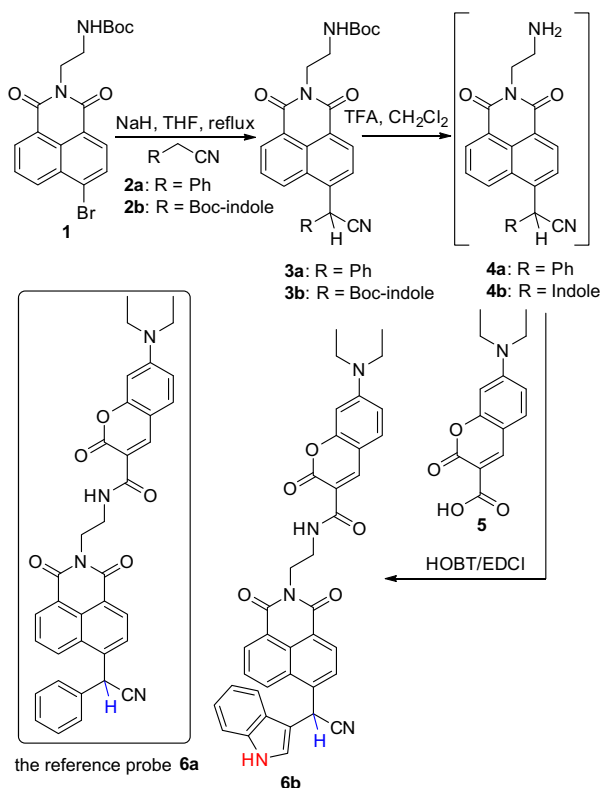
Scheme 1. Design strategies for the FRET-based fluorescent probes.

condensation of *N*-Boc-butyl-4-bromo-1,8-naphthalimide (**1**) with substituted 2-acyl acetonitrile (**2**) according to our recently reported procedure.<sup>13</sup> Subsequent deprotection of the Boc group provided **4**, which was further coupled with coumarin acid **5** by a standard EDCI-mediated amide coupling to produce the target probes **6**.<sup>14</sup> The structures of **6a** and **6b** were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, HRMS spectroscopy (Figs. S1–S13).

First, the chromogenic behavior of probes **6a** and **6b** in THF<sup>15</sup> upon the addition of different anions was studied (Fig. 1a and c). When tetrabutylammonium cyanide (TBACN) was added, new peaks at 646 and 616 nm were observed in the UV–visible spectra of probes **6a** or **6b**, respectively. A larger red-shift was observed ( $\approx 311$  nm and  $\approx 281$  nm) when TBACN was added to **6a** and **6b**, respectively, and may be attributed to the presence of an enhanced  $\pi$ -conjugation network involving the complex of [probes + CN<sup>-</sup>]

through the intermolecular hydrogen bonding.<sup>16</sup> After the addition of 4.0 or 5.0 equiv of CN<sup>-</sup>, an instantaneous colorimetric change from colorless to dark blue (Fig. 1a for **6a** and 1c for **6b**, inset, naked-eye detection) was observed. To validate the selectivity of sensors **6a** and **6b**, the same tests were also conducted using F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, AcO<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, OH<sup>-</sup> ions. Except for the stronger basic anions (F<sup>-</sup>, OH<sup>-</sup>, and AcO<sup>-</sup>), none of other anions induced any significant changes in the UV–visible spectra of probes **6a** and **6b**. This indicates that the probes show a very typical response based on anion basicity. Compared with **6a**, the high selectivity of **6b** may be attributed to its dual binding sites of CHCN and NH, which can competitively bind with cyanides. It was further highlighted by the interference experiment and no significant interference was observed (Fig. S14). Moreover, the addition of increasing concentrations of CN<sup>-</sup> ion resulted in a dramatic color changes from colorless to dark blue, which is associated with the simultaneous growth of a new peaks at 646 nm (**6a**) and 616 nm (**6b**) in THF and is consistent with our previous reported<sup>12c</sup> (Fig. 2b and d). This indicates that a complex of [probes + CN<sup>-</sup>] might have formed through hydrogen bonding (CH $\cdots$ CN<sup>-</sup>) interaction, which results in a new charge transfer complex with a novel spectral signal. The absorbance intensity of probes **6a** or **6b** was saturated when 4.0 or 5.0 equiv of CN<sup>-</sup> was added to the THF solution, and the color changes of probes **6a** or **6b** from colorless to dark blue may be attributed to the drastic change in electron rearrangement induced by proton transfer from probes **6a** or **6b** (predominantly polarized CHCN donor) to CN<sup>-</sup> ions. After **6b** is saturated with CN<sup>-</sup> ions, the absorbance decrease slightly, and it may be ascribed to the indole NH deprotonation induced by excess CN<sup>-</sup>. The detection limits of probes **6a** or **6b** was determined to be 1.10  $\mu$ M and 6.91  $\mu$ M, respectively (see Figs. S15 and S16). The spectral response of **6a** and **6b** in the absence and presence of CN<sup>-</sup> at different pH was also evaluated (Fig. S17). Compared to **6a**, probe **6b** showed CN<sup>-</sup> detection at a moderate range of pH values (pH 4–10), indicating that the dual-site controlled probe **6b** shows more advantage than probe **6a**.

We then used fluorescence spectroscopy to investigate the behavior of the **6a** or **6b** probes in the presence of CN<sup>-</sup> ions. Due to the occurrence of potential FRET on, the naphthalimide group can transfer energy to the coumarin, so the probe **6a** only shows the emission fluorescence of the coumarin group ( $\lambda_{em} = 450$  nm, Fig. 2a). When CN<sup>-</sup> ions were added to a solution of **6a**, a significant decrease in the fluorescence intensity at 450 nm ( $\lambda_{ex} = 350$  nm) was observed, indicating that the FRET process was prohibited<sup>10</sup> as it was affected by the ICT process induced by CH $\cdots$ CN<sup>-</sup> hydrogen bonding.<sup>17</sup> None of the other anions (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>,

Scheme 2. Synthesis of the target probe **6b** and its reference probe **6a**.

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