Tetrahedron 72 (2016) 5620-5625

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

A simple AIE-based chemosensor for highly sensitive and selective detection of Hg²⁺ and CN⁻

Yiru Li^a, Haitao Zhou^a, Wei Chen^a, Guangchen Sun^a, Lu Sun^b, Jianhua Su^{a,*}

^a Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai, 200237, PR China ^b Institute of Modern Optics, Nankai University, Tianjin, 300071, PR China

ARTICLE INFO

Article history: Received 23 May 2016 Received in revised form 11 July 2016 Accepted 22 July 2016 Available online 22 July 2016

Keywords: AIE Chemosensor Hg²⁺ CN

ABSTRACT

A novel red-emitting chemosensor BCTT has been developed for the detection of Hg²⁺ and CN⁻ in DMFwater solution with high sensitivity and selectivity. It exhibited a 'turn-on' fluorescence upon binding with Hg²⁺ based on its AIE properties and a 'turn-off' response to CN⁻ due to the nucleophilic addition of CN⁻ to the dicyanovinyl group with visible color changing from yellow to colorless. Remarkably, the detection limits for Hg^{2+} and CN^- were 6.6 nM and 0.11 μ M, respectively, which are much lower than the regulated limits in drinking water, promoting BCTT as a promising candidate in practical applications. © 2016 Published by Elsevier Ltd.

1. Introduction

Among the various metal ions and anions, Hg^{2+} and CN^{-} are considered to be especially deleterious to human health and natural environment. Hg^{2+} , one of the most toxic heavy metal ions, mostly released by human activities such as coal-fired power stations, primary metals production, and the chlor-alkali industry,¹ is known to be accumulated over time through the food chain. causing significant damage to organs such as brain, kidneys, liver and nervous system.² Similarly, cyanide is a kind of extremely poisonous compounds, existing in certain plants, such as cassava. the seeds of several fruits, cigarette smoke, and the combustion products of synthetic materials,³ and is commonly utilized in industries such as precious metal mining, metal plating shops, steel mills, and plastic and fertilizer plants.⁴ Cyanide ions can form a stable complex with cytochrome *c* oxidase, which disrupts the function of this enzyme, resulting in cytotoxic hypoxia and cellular asphyxiation. Moreover, anaerobic metabolism induced by cyanide leads to accumulation of lactate in the blood. The combined effects of hypoxia and lactate acidosis disturb the central nervous system, resulting in respiratory arrest and even death.³⁻

Thus, given the widespread occurrence and extreme toxicity of Hg²⁺ and CN⁻, the selective and sensitive determination of both ions in various samples is of great importance for lives on the earth. Traditional methods including atomic absorption spectroscopy

applications.¹⁶ It is because that blue florescence is strongly attenuated by a biological specimen while red fluorescence corresponds to the biological specimen's transparency window, producing high penetration depth. Hence a novel TPA-based red emitting probe BCTT with AIE

properties was designed and synthesized for detecting both Hg²⁺

(AAS), atomic fluorescence spectrometry (AFS), and inductively coupled plasmamass spectrometry (ICP-MS) for Hg²⁺detection,⁶

and potentiometric, chromatographic, and flow injection tech-

niques for CN⁻ analysis are usually high cost, time-consuming and

require sophisticated instruments.^{7,8} In contrast, optical detection

based on absorption or fluorescence which takes advantages of simplicity and low detection limit has been widely studied and

developed in recent years.⁹ Consequently, tremendous sensors for

detecting Hg²⁺ or CN⁻ have been reported, however, sensors with responsibility for both are relatively rare to date.¹⁰ Considering the

fluorescence quenching effect of Hg²⁺, the turn-on fluorescent

chemosensors based on AIE phenomenon induced by metal ion

complexation are more favorable for sensitive detection and wide use.¹¹⁻¹⁴ Otherwise, cyanide chemosensors are tended to take ad-

vantage of the unique nucleophilicity of cyanide to realize recog-

nition through the bond-formation reaction between the probing

molecule and cyanide anions, minimizing the interference of other anions.¹⁵ Herein, thymine was chosen as an acceptor for its affinity

with Hg²⁺ and the dicyano-vinyl group was selected as a reactive

moiety for CN⁻. Moreover, due to the strong electron-withdrawing

property, the dicynao-vinyl group can also cause a considerable

bathochromic-shift of emission, making it feasible in biological







^{*} Corresponding author. E-mail address: bbsjh@ecust.edu.cn (J. Su).

and CN⁻, which contains two thymine groups and a dicyano-vinyl group as coordination/reaction sites. The probe was expected to be a dual-functional detector with high selectivity and sensitivity, which has potential in practical applications.

2. Results and discussion

2.1. Synthesis

The synthetic route of BCTT was depicted in Scheme 1. The intermediates 1 and 2 were synthesized according to the reported literature.^{17,18} Compounds 3, 4 and 5 were obtained through simple reactions. The target compound BCTT was synthesized and confirmed by ¹H NMR, ¹³C NMR and High-resolution mass spectroscopy (HRMS).



Scheme I. Structure and synthetic route of Derit.Schem

2.2. AIE performance of BCTT

To investigate the AIE property of BCTT, we tested its absorption and emission spectra in DMF-H₂O mixtures with different water fraction. As shown in Fig. 1a, BCTT was almost nonemissive in pure DMF solution and low water content solution. However, the fluorescence intensity at 650 nm increased dramatically when water content increased to 60 vol %, and reached its maximum with 120fold enhancement in intensity when the water fraction reached 80 vol %. BCTT was therefore AIE active. Further increase in water fraction resulted in a slight decrease of fluorescence intensity, which could be ascribed to the formation of amorphous aggregates. What's more, a slight red shift and intensity decrease could be observed in absorption spectra (Fig. S1), which may be caused by the increasing solvent polarity and accumulation of molecules.

2.3. Optical response to Hg²⁺

It is known that thymine can bind with Hg^{2+} sensitively and selectively, therefore we investigated the absorbance and fluorescence responses of the probe to different amounts of Hg^{2+} . Considering the requirement of the test solvent with low biotoxicity and high water content but not affecting the probe's fluorescence for further biological application, we tested the sensing behavior of BCTT towards Hg^{2+} in DMF-H₂O solutions with different water percentage (Fig. S2, Fig. 2a), and the mixture of DMF-H₂O (13:12, v/v)



Fig. 1. a) The fluorescence spectra of BCTT (10.0 μ M) in DMF-water mixtures with different water fractions (f_w). b) Plots of relative PL intensity (I/I_0) of BCTT at 645 nm versus the composition of DMF-water mixtures of BCTT. I_0 =PL intensity in pure DMF solution (f_w =0). Inset: fluorescence photos of BCTT in DMF-H₂O mixtures at f_w =0 (left) and 80% (right) taken under 365 nm UV illumination from a hand-held UV lamp.

was proved to be the best choice as test solution. Besides, SDS (Sodium Dodecyl Sulfonate) (1.0 mM) was added to make the complexing between probe and Hg^{2+} faster and more easily.¹⁹

The fluorescence spectra of the probe in the presence of a serious of concentrations of Hg²⁺ was shown in Fig. 2a. The probe has a weak emission at ca. 600 nm, then upon the addition of Hg^{2+} , the fluorescence intensity of BCTT started to increase gradually accompanied by a bathochromic shift of 50 nm, and reached the maximum, which was about 20 times stronger than the original value, after the treatment of 1.0 equiv Hg²⁺ (Fig. S3a). A red fluorescence could be observed by naked eye under a UV lamp at 360 nm. Moreover, an approximate linear relationship between the fluorescence intensity of probe and the concentration of Hg²⁺ in the range of 1.5-8.8 µM was exhibited in Fig. 2b. Remarkably, the detection limit of BCTT was calculated to be 6.6 nM by the formula $3\sigma/$ |k|, which is much lower than the limit of Hg²⁺ in drinking water (2 ppb, ca. 10 nM) set by the US EPA,²⁰ indicating the high sensi-tivity of the probe towards Hg^{2+} . As for the change of absorbance of probe under the titration of Hg^{2+} , a slight red shift and about a quarter intensity decline caused by the aggregation of BCTT and reduced solubility was observed when complexation arrived at the saturation point (Fig. S3b).

The probes with fluorescence enhancement due to aggregation induced by coordination of thymine units with Hg^{2+} have been reported previously,^{13,14} and the proposed mechanism is schematically illustrated in Scheme 2. Firstly, after addition of Hg^{2+} , BCTT aggregated in the solution causing the fluorescence increase, which could be proved by corresponding absorption spectrum and SEM analysis. Fig. S3b shows the absorption changes after titration with mercury ion. The absorption band at 440 nm became weak and intensity in the range of 480–580 nm increased gradually,



Fig. 2. a) Fluorescence spectra of BCTT in DMF-H₂O (13:12, v/v) (10.0 μ M) upon addition of 0–1.2 equiv of aqueous Hg²⁺, λ_{ex} =440 nm. Inset: fluorescence photos of BCTT with different amount of Hg²⁺ (left: none; right: 1.2 equiv Hg²⁺). b) The fluorescence intensity (I_{645}) as a linear function of Hg²⁺ concentration (from 1.5 to 8.8 μ M), λ_{ex} =440 nm, λ_{em} =645 nm, σ =0.10. The standard deviation (σ) was obtained by fluorescence intensity (10-times scanning without addition of Hg²⁺). The detection limit was calculated to be 6.6 nM by the formula ($3\sigma/|k|$).

indicating the aggregation of the probe. Moreover, the SEM image (Fig. S4) reveals the formation of aggregate in the solution of BCTT with 1.0 equiv of Hg²⁺. In addition, the Job's plot (Fig. S5) presented a maximum fluorescence intensity as the ratio *x* was 0.5, and MALDI-TOF mass spectrum (Fig. S6) of probe in the presence of Hg²⁺ showed a signal at m/z=970.3216, coinciding with that of [BCTT/Hg²⁺-H⁺]. Above evidence suggested a 1:1 stoichiometry of the complexes between probe and Hg²⁺.

In order to examine the selectivity of this assay for Hg^{2+} , we measured the fluorescent responses of the probe to various metal ions. It can be seen from Fig. 3, the addition of 1.0 equiv of Hg^{2+} could produce a notable fluorescence enhancement of the probe, while 50.0 equiv of other metal ions did not induce the apparent fluorescence increase. Subsequently, competition experiments were carried out to ensure the potential application of the probe for practical use. The fluorescent intensity of BCTT in the presence of 1.0 equiv Hg^{2+} and 50.0 equiv competing metal ions changed little comparing to that with the addition of Hg^{2+} only, indicating that our proposed probe is highly selective for Hg^{2+} .

2.4. Optical response to CN⁻

In order to investigate the ability of BCTT to detect CN⁻, the cyanide titration experiment was carried out in DMF-H₂O solutions with different water fraction (Figs. S7–S10, Fig. 4), with the assistance of CTAB (Hexadecyl trimethyl ammonium Bromide) (1.0 mM). According to results, BCTT was most sensitive towards CN⁻ in DMF- H_2O (1:19, v/v). As shown in Fig. 4, the initial solution emitted red fluorescence located at 645 nm because of the AIE property of BCTT. The visual color of yellow corresponding to main absorption band centered at 440 nm could be observed distinctly by naked eye as well. Afterwards, the sensor immediately responded with dramatic color and fluorescence changes when cyanide was added to the solution of BCTT. As shown in Fig. 4a, the absorption band at 440 nm gradually decreased with the addition of CN⁻ and eventually disappeared after 7.8 equiv of CN⁻ was added, which was accompanied by the color change from yellow to colorless, suggesting the complete addition reaction between dicyanovinyl and CN⁻.

Meanwhile, the fluorescence intensity reduced gradually with increasing amounts of CN⁻. As expected, the red fluorescence finally quenched when the titration reached its end point (Fig. 4b). Notably, the detection limit for CN⁻ using fluorescence intensity changes was estimated to be 0.11 μ M, which is far lower than the WHO guideline of 1.9 μ M (Fig. S10a).²¹

The reaction process of CN⁻ undergoing conjugate addition to the 1,1-dicyano-vinyl group to produce a stabilized anionic adduct has been studied in previous literature.^{22,23} Thus, the ¹H NMR titration of BCTT upon addition of 0–1.0 equiv of cyanide in DMSO- d_6 was performed to confirm this sensing process. It can be seen from Fig. 5 that the vinylic proton (Ha) at 8.14 ppm gradually decreased with progressive addition of CN⁻ and eventually vanished when 1.0 equiv of cyanide was added, implying the completion of nucleophilic addition. Concurrently, a new signal appeared at 4.41 ppm attached to Hb. Naturally, the aromatic proton signals all upfield shifted due to the broken conjugation between the diacyanovinyl group and triphenylamine framework. What's more, the



Scheme 2. Proposed schematic illustration of the coordination between BCTT and Hg²⁺.Scheme 2



Fig. 3. PL Intensities at 645 nm of BCTT (10.0 μ M) in DMF-H₂O (13: 12, v/v) in the absence of Hg²⁺ and in the presence of various ions (1.0 equiv for Hg²⁺ and 50.0 equiv for other ions, λ_{ex} =440 nm, black bar portion) and in the mixture of 50.0 equiv of other metal ions with 10.0 μ M of Hg²⁺ (gray bar portion).



Fig. 4. a) Absorption and b) fluorescence spectra of BCTT in DMF-H₂O (1:19,v/v) (10.0 μ M) upon addition of 0–7.8 equiv of aqueous CN⁻; λ_{ex} =440 nm. Inset: photos of BCTT with different amount of cyanide (left: none; right: 7.8 equiv of cyanide).



Fig. 5. Partial ¹H NMR spectra of BCTT (5 mM) in DMSO- d_6 with different equivalent of CN⁻.

¹³C NMR spectra of BCTT in CDCl₃ after addition of 1.0 equiv CN⁻ was conducted (Fig. S11). It can be seen that signals at around 157 and 73 ppm belonging to vinylic carbons disappeared and shifted to 23 and 17 ppm after addition of CN⁻ and the signal of added cyano

group appeared at 140 ppm, implying the nucleophilic addition of CN⁻ with dicyano-vinyl group. Furthermore, 1:1 stoichiometric reaction between BCTT and cyanide could be proved by Benesi-Hildebrand plot of absorbance at 440 nm upon addition of cyanide (Fig. S10b), which revealed a linear correlation between 1/ ΔA_{440} and 1/[CN⁻], and MS (ESI) spectra after treatment of CN⁻, showing a signal of *m*/*z*=795.3624 which was exactly coincided with that of [BCTT+CN] (Fig. S12).

Moreover, the interference studies were undertaken in the identical condition to examine the selectivity of BCTT. As described in Fig. 6, the absorbance intensity at 440 nm and fluorescence intensity at 645 nm remained almost unchanged in the presence of 400.0 equiv of those ions, sufficiently showing the excellent selectivity for CN^- . In addition, the sensing abilities of BCTT for cyanide was not affected by the treatment of excessive other anions, indicating its potential political application for cyanide sensing in aqueous medium.

3. Conclusion

In summary, a novel fluorescent probe BCTT with red emission centered at 645 nm, combining a dicyanovinyl group and triphenylamine skeleton with thymine, has been successfully synthesized for the detection of mercury and cyanide ions in DMF-water solution containing SDS and CTAB, respectively. BCTT exhibited a fluorescence enhancement upon addition of Hg²⁺ due to the coordination between thymine groups and Hg²⁺ based on its AIE



Fig. 6. a) Absorbance intensities at 440 nm and b) PL Intensities at 645 nm of BCTT (10.0 μ M) in DMF-H₂O (1:19, v/v) in the absence of CN⁻ and in the presence of various ions (8.0 equiv for CN⁻ and 400.0 equiv for other anions, λ_{ex} =440 nm, gray bar portion) and in the mixture of 4 M of other anions with 80.0 mM of CN⁻ (black bar portion).

properties. What's more, the probe could detect CN^- with the quenched red fluorescence and decreased absorbance intensity, presenting a color change from yellow to colorless, which could be observed by naked eye. Both the sensing processes were monitored by ¹H NMR or MS spectra to reveal the mechanisms of Hg²⁺ induced aggregation and CN^- triggered nucleophilic addition. It is mentionable that BCTT showed superb selectivity and sensitivity towards Hg²⁺ and CN^- in the presence of other interfering ions, which were also proved by the competition experiments. It is therefore that probe BCTT could serve as a high sensitive and selective detector for both Hg²⁺ and CN⁻, with the detection limits as low as 6.6 nM and 0.11 μ M for Hg²⁺ and CN⁻, respectively. Our work opens up a new avenue for the research of dual-functional fluorescent probes for cations and anions.

4. Experimental section

4.1. Materials

Compound **1** and **2** were synthesized according to previous literature. Other reactants were purchased commercially and used as received without further handling. The salts used in stock solutions of metal ions were NaCl, KCl, AlCl₃, AgNO₃, CaCl₂, CoCl₂· 6H₂O, CrCl₃· 6H₂O, CuCl₂· 2H₂O, FeCl₃· 6H₂O, Hg(ClO₄)₂· 3H₂O, MnCl₂· 4H₂O, NiCl₂· 6H₂O, PbCl₂, ZnCl₂, and the solutions of anions were prepared from the corresponding sodium salts except that the hydroxide ion and cyanide anion were in the form of tetrabuty-lammonium (TBA) salts. Water used in tests was double distilled water. All the organic solvents were dried with 4 Å molecular sieves prior to use and DMF treated with calcium hydride was further distilled under reduced pressure for main experiments.

4.2. Instruments

¹H NMR and ¹³C NMR spectra were recorded on Brucker AM-400 spectrometers using DMSO- d_6 as solvent and tetramethylsilane (TMS, δ =0 ppm) as internal standard. Mass spectra (MS) were obtained on a Waters LCT Premier XE spectrometer. The UV–vis absorption spectra and PL spectra were performed on a Varian Cray 500 spectrophotometer and a Varian Cray Eclipse, respectively.

4.3. Synthesis

4.3.1. 4-Methoxy-N-(4-methoxyphenyl)-N-phenylaniline (1). 4iodoanisole (7.20 g, 30.76 mmol) and aniline (1.14 mL, 12.49 mmol) were dissolved in a round-bottom flask in 50 mL toluene, and ophenanthroline (0.45 g, 2.30 mmol), cuprous iodide (0.48 g, 2.52 mmol) and potassium hydroxide (5.60 g, 100.00 mmol) were added to the solution. The mixture was refluxed under N₂ atmosphere for 12 h and then treated according to previous literature to obtain the compound **1** as a white solid (2.50 g). Yield: 65.6%.¹⁷

4.3.2. 4-(Bis(4-methoxyphenyl)methyl)benzaldehyde(2). Compound 1 (2.00 g, 6.55 mmol) was treated with POCl₃ in DMF according to the reported method to afford the compound 2 as a yellow liquid (2.00 g). Yield: 91.7%.¹⁸

4.3.3. 4-(Bis(4-hydroxyphenyl)amino)benzaldehyde (**3**). A solution of compound **2** (2.00 g, 6.00 mmol) in dichloromethane was added with BBr₃ (4.51 g, 6.00 mmol) (1.0 M solution in dichloromethane) at 0 °C and stirred under N₂ atmosphere for 30 min. The reaction mixture was stirred for another 24 h at room temperature and poured into water and then extracted with ethyl acetate (3×50 mL). The extract was dried (NaSO₄) and concentrated. The residue was chromatographed on silica gel with ethyl acetate/petroleum (2: 1) to give compound **3** (1.80 g) as a yellow liquid. Yield: 98.3%. ¹H NMR

(DMSO- d_6 , 400 MHz, TMS), δ : 9.67 (s, 1H), 9.59 (s, 2H), 7.61 (d, J=9.2 Hz, 2H), 7.09 (d, J=8.8 Hz, 4H), 6.81 (d, J=8.8 Hz, 4H), 6.62 (d, J=8.8 Hz, 2H). ¹³C NMR (DMSO- d_6 , 100 MHz), δ : 189.99, 155.81, 154.15, 136.70, 131.45, 128.82, 126.68, 116.66, 114.76. HRMS (m/z): [M+H]⁺ calcd for: C₁₉H₁₆NO₃, 306.1130, found: 306.1129.

4.3.4. 4-(Bis(4-((6-bromohexvl)oxv)phenvl)amino)benzaldehvde (4). The solution of 3 (1.80 g. 5.90 mmol) and 1.6-dibromohexane (7.20 g, 29.48 mmol) in acetonitrile (50 mL) added with K₂CO₃ (4.07 g, 29.48 mmol) was refluxed overnight under N₂ atmosphere. The reaction mixture was concentrated, dissolved in dichloromethane, washed with water, dried over anhydrous NaSO₄, and concentrated. The residue was chromatographed on silica gel with petroleum/ethyl acetate (7:1) to get compound 4 (2.50 g) as a yellow liquid. Yield: 67.2%. ¹H NMR (DMSO- d_6 , 400 MHz, TMS), δ : 9.69 (s, 1H), 7.63 (d, *I*=9.2 Hz, 2H), 7.16 (d, *I*=8.8 Hz, 4H), 6.96 (d, J=9.2 Hz, 4H), 6.68 (d, J=8.8 Hz, 2H), 3.94 (t, J=6.4 Hz, 4H), 3.52 (t, J=6.8 Hz, 4H), 1.85–1.78 (m, 4H), 1.72–1.69 (m, 4H), 1.47–1.39 (m, 8H). ¹³C NMR (DMSO-*d*₆, 100 MHz), δ: 190.07, 156.60, 153.66, 137.89, 131.29, 128.35, 127.00, 115.68, 115.26, 67.50, 35.03, 32.16, 28.49, 27.27, 24.66. HRMS (*m/z*): [M+H]⁺ calcd for: C₃₁H₃₈Br₂NO₃, 630.1218, found: 630.1220.

4.3.5. 4-(Bis(4-((6-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)hexyl)oxy)phenyl)amino)benzaldehyde (5). To the solution of 4 (2.50 g, 3.96 mmol) in DMF was added 5-methyluracil (3.00 g, 23.40 mmol) and K₂CO₃ (5.47 g, 39.60 mmol), and stirred at 60 °C under N₂ atmosphere for 36 h. After the reaction, DMF was removed under reduced pressure. The mixture was dissolved in dichloromethane and washed with water for three times. The oil layer was dried (anhydrous Na₂SO₄), concentrated, and chromatographed on silica gel with ethyl acetate/petroleum (3: 1) to give compound **5** (1.50 g) as bright yellow liquid. Yield: 52.4%. ¹H NMR (DMSO-d₆, 400 MHz, TMS), δ: 11.22 (s, 2H), 9.70 (s, 1H), 7.65 (d, J=8.8 Hz, 2H), 7.54 (s, 2H), 7.18 (d, J=9.2 Hz, 4H), 6.97 (d, J=9.2 Hz, 4H), 6.68 (d, J=8.8 Hz, 2H), 3.95 (t, J=6.4 Hz, 4H), 3.62 (t, J=7.2 Hz, 4H), 1.74 (s, 6H), 1.73-1.68 (m, 4H), 1.63-1.56 (m, 4H), 1.45-1.40 (m, 4H), 1.35–1.27 (m, 4H). ¹³C NMR (DMSO-*d*₆, 100 MHz), δ: 190.13, 164.26, 156.62, 153.69, 150.84, 141.42, 137.88, 136.18, 131.34, 128.41, 126.97, 115.69, 115.22, 108.34, 107.13, 67.52, 47.04, 28.46, 28.37, 25.52, 25.16, 11.90. HRMS (*m/z*): [M+H]⁺ calcd for: C₄₁H₄₈N₅O₇, 722.3554, found: 722.3550.

4.3.6. 2-(4-(Bis(4-((6-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)hexyl)oxy)phenyl)amino)benzylidene)malononitrile (BCTT). Ammonium acetate (58.59 mg, 0.76 mmol) was added to the solution of compound 5 (0.50 g, 0.69 mmol) and malononitrile (0.46 g, 6.91 mmol) in acetic acid. The mixture was refluxed under N₂ atmosphere for 12 h. Upon cooling, the mixture was poured into cold water to give a red precipitate. The crude product was collected by suction filtration and purified by silica gel column chromatography (petroleum ether/ethyl acetate=1:3 v/v) to afford the compound BCTT as a dark red solid (0.30 g). Yield: 56.4%. ¹H NMR (DMSO- d_6 , 400 MHz, TMS), δ: 11.20 (s, 2H), 8.14 (s, 1H), 7.77 (d, *J*=9.2 Hz, 2H), 7.54 (s, 2H), 7.22 (d, J=9.2 Hz, 4H), 6.99 (d, J=8.8 Hz, 4H), 6.68 (d, J=8.8 Hz, 2H), 3.96 (t, J=6.4 Hz, 4H), 3.62 (t, J=7.2 Hz, 4H), 1.74 (s, 6H), 1.71-1.68 (m, 4H), 1.63-1.55 (m, 4H), 1.47-1.40 (m, 4H), 1.34-1.29 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz), δ: 164.28, 157.83, 157.36, 154.17, 150.94, 140.33, 137.63, 133.20, 128.18, 121.66, 116.54, 115.72, 115.57, 110.70, 73.89, 67.90, 48.41, 29.07, 28.98, 26.14, 25.71, 12.36. HRMS (m/ *z*): [M+H]⁺ calcd for: C₄₄H₄₈N₇O₆, 770.3666, found: 770.3674.

Acknowledgements

This work was supported by National Natural Science Foundation of China (20772031), the National Basic Research 973 Program (2006CB806200), the Fundamental Research Funds for the Central Universities (WJ0913001), and the Scientific Committee of Shanghai (10520709700).

Supplementary data

Supplementary data (The characterization (NMR and MS) of BCTT) related to this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.07.054.

References and notes

- Díaz de Greñu, B.; García-Calvo, J.; Cuevas, J.; García-Herbosa, G.; García, B.; Busto, N.; Ibeas, S.; Torroba, T.; Torroba, B.; Herrera, A.; Pons, S. Chem. Sci. 2015, 6, 3757–3764.
- Minami, T.; Sasaki, Y.; Minamiki, T.; Koutnik, P.; Anzenbacher, P., Jr.; Tokito, S. Chem. Commun. (Camb.) 2015, 17666–17668.
- 3. Wang, F.; Wang, L.; Chen, X.; Yoon, J. Chem. Soc. Rev. 2014, 43, 4312-4324.
- Rosentreter, J. J.; Timofeyenko, Y. G.; Moreno, M. Microchem. J. 2015, 12, 11917–11921.
- Lee, J. H.; Jang, J. H.; Velusamy, N.; Jung, H. S.; Bhuniya, S.; Kim, J. S. Chem. Commun. (Camb.) 2015, 7709–7712.
- 6. Kim, H. N.; Ren, W. X.; Kim, J. S.; Yoon, J. Chem. Soc. Rev. 2012, 41, 3210-3244.
- 7. Badugu, R.; Lakowicz, J. R.; Geddes, C. D. J. Am. Chem. Soc. 2005, 127, 3635–3647.

- 8. Xie, D.-X.; Ran, Z.-J.; Jin, Z.; Zhang, X.-B.; An, D.-L. Dyes Pigm. 2013, 96, 495–499.
- 9. Rosentreter, J. J.; Timofeyenko, Y. G.; Moreno, M. *Microchem. J.* **2015**, *119*, 17–21.
- Gwona, S.-Y.; Rao, B. A.; Kim, H.-S.; Son, Y.-A.; Kim, S.-H. Spectrochim. Acta, Part A 2015, 144, 226–234.
- 11. Chen, W.; Zhang, Z.; Li, X.; Ågren, H.; Su, J. RSC Adv. 2015, 5, 12191–12201.
- 12. Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Tang, B. Z.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D. *Chem. Commun.* **2001**, 1740–1741.
- 13. Liu, L.; Zhang, G.; Xiang, J.; Zhang, D.; Zhu, D. Org. Lett. 2008, 10, 4581–4584.
- Zhang, H.; Qu, Y.; Gao, Y.; Hua, J.; Li, J.; Li, B. Tetrahedron Lett. 2013, 54, 909–912.
 Wei, T.-T.; Zhang, J.; Mao, G.-J.; Zhang, X.-B.; Ran, Z.-J.; Tan, W.; Yu, R. Anal.
- Methods **2013**, 5, 3909.
- Allain, C.; Schmidt, F.; Lartia, R.; Bordeau, G.; Debuisschert, C. F.; Charra, F.; Tauc, P.; Fichou, M. T. ChemBioChem 2007, 8, 424–433.
- Rakstys, K.; Abate, A.; Dar, M. I.; Gao, P.; Jankauskas, V.; Jacopin, G.; Kamarauskas, E.; Kazim, S.; Ahmad, S.; Gratzel, M.; Nazeeruddin, M. K. J. Am. Chem. Soc. 2015, 137, 16172–16178.
- 18. Shi, D.; Cao, Y.; Pootrakulchote, N.; Yi, Z.; Xu, M.; Zakeeruddin, S. M.; Gratzel, M.; Wang, P. J. Phys. Chem. C 2008, 112, 17478–17485.
- Mallick, A.; Mandal, M. C.; Haldar, B.; Chakrabarty, A.; Das, P.; Chattopadhyay, N. J. Am. Chem. Soc. 2006, 128, 3126–3127.
- Voutsadaki, S.; Tsikalas, G. K.; Klontzas, E.; Froudakis, G. E.; Katerinopoulos, H. E. Chem. Commun. (Camb.) 2010, 3292–3294.
- 21. Lin, Q.; Fu, Y.-P.; Chen, P.; Wei, T.-B.; Zhang, Y.-M. Tetrahedron Lett. 2013, 54, 5031–5034.
- 22. Cheng, X. H.; Zhou, Y.; Qin, J. G.; Li, Z. ACS Appl. Mater. Interfaces 2012, 4, 2133–2138.
- 23. Lee, C. H.; Yoon, H. J.; Shim, J. S.; Jang, W. D. Chem.-Eur. J. 2012, 18, 4513-4516.