

Supporting Information

A ratiometric fluorescent probe of novel HBI derivative for rapid detection of trifluoroborate

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1 EXPERIMENTAL

1.1 Materials and Methods

5-Bromosalicylaldehyde, ethyltrimethylsilane, o-phenylenediamine, PdCl₂(PPh₃)₂, PPh₃, CuI, trifluoroborate ethyl ether solution, bis(pinacolato)diboron, boric acid, phenylboronic acid, allyl trifluoroborate potassium, hydrogen fluoride, trifluoroacetic acid, potassium fluoride, tetrabutylammonium fluoride and organic solvents were purchased from Shanghai Aladdin Bio-Chem Technology Co, LTD. Unless otherwise stated, commercial reagents were used without further purification. Tetrahydrofuran and triethylamine were distilled from standard drying agents. The testing solvents were prepared with dichloromethane.

1.2 General Instrumentation

Emission spectra were performed on a Fluorescence spectrometer (F-4600). Error limits were estimated: λ (± 1 nm); τ ($\pm 10\%$); ϕ ($\pm 10\%$). IR spectra were recorded on Vario EL.III Fourier transform infrared spectrometer (Elementar, Germany). ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on Bruker Avance AV400 spectrometer (Bruker, Billerica, MA, USA) unless otherwise noted. The chemical shifts (δ) were quoted in parts per million from tetramethylsilane for ¹H and for ¹³C spectroscopy.

1.3 Characterization of HTEP and BTEP

The ¹H NMR and ¹³C NMR spectroscopy of **HTEB** shown as Figure S1 and S2. ¹H NMR (400 MHz, CDCl₃) δ 11.04 (s, 1H), 9.78 (s, 1H), 7.64 (d, $J = 2.1$ Hz, 1H), 7.53 (dd, $J = 8.7, 2.1$ Hz, 1H), 6.87 (d, $J = 8.7$ Hz, 1H), 0.18 (s, 9H); ¹³C NMR (400 MHz, CDCl₃) δ 196.2, 161.6, 140.2, 137.5, 120.4, 118.0, 115.2, 103.2, 93.9, 0.0. The ¹H NMR spectrum exhibits the typical signals for **HTEB**. The chemical shift of CHO

have a peak splitting of 9.78 ppm, and the chemical shift of -OH proton shifted down field at 11.04 ppm. The dd peak range from 7.52 to 7.54 ppm corresponding to the aromatic hydrogens at the ortho- position of -CHO group. The d peaks of 6.87 and 7.64 ppm represent of the aromatic hydrogen at the meta- and ortho- position of the -CHO group, respectively. The single peak at 0.18 ppm was the typical signal of the aromatic hydrogen at the Trimethylsilyl group. The ^{13}C NMR spectrum exhibits 10 peaks, which fully agree with the proposed structure for **HTEB**. The FT-IR spectra shown as Fig. S3, The hydroxyl groups, alkynyl groups, aldehyde groups in the **HTEB** molecule is confirmed by characteristic absorption peaks at 3210 nm, 2150 nm, and 1667 nm.

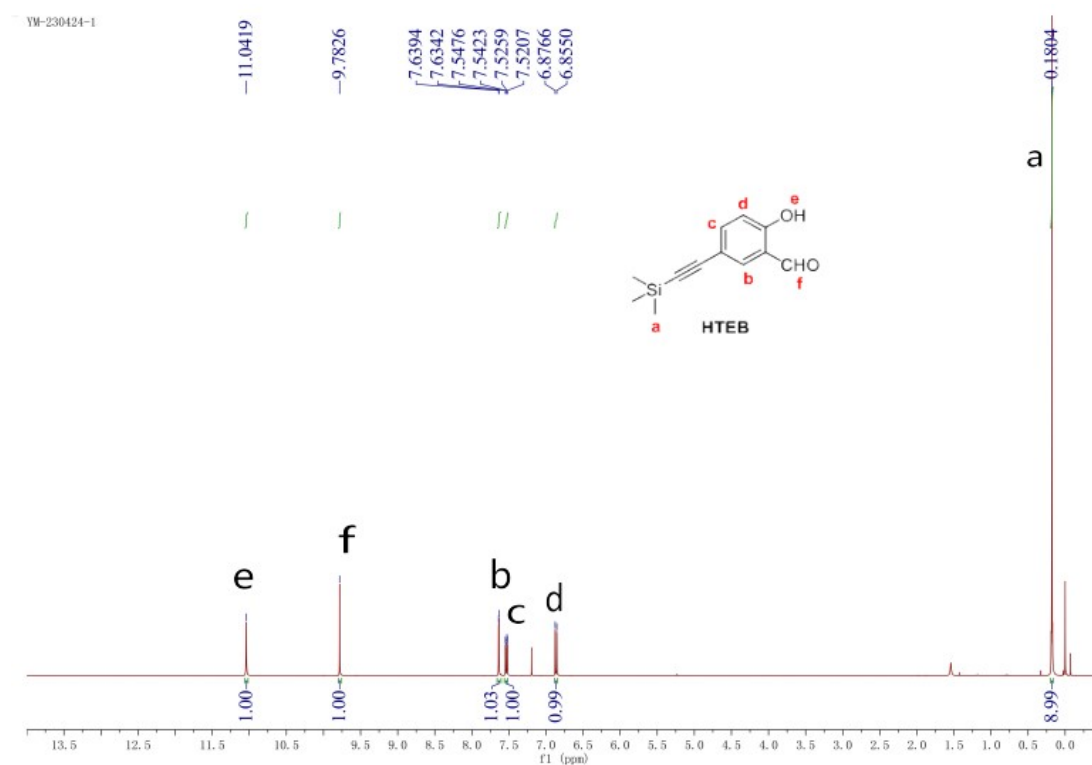


Figure S1. ^1H NMR spectrum (400 MHz, CDCl_3) of **HTEB**

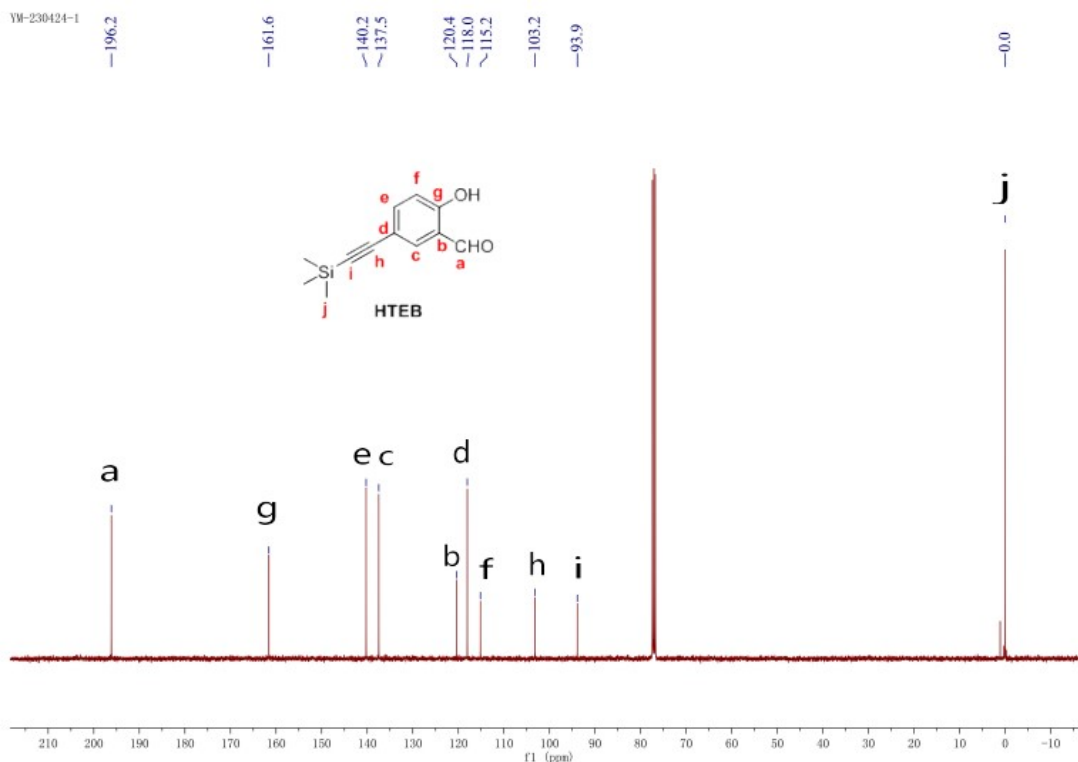


Figure S2. ^{13}C NMR spectrum (100 MHz, CDCl_3) of HTEB

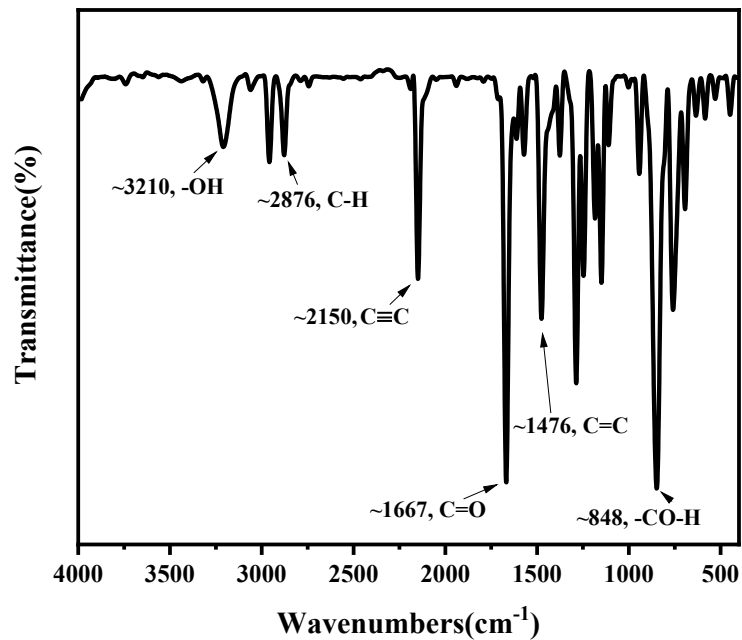


Figure S3. FT-IR spectrum of HTEB

The ^1H NMR and ^{13}C NMR spectroscopy of BTEP shown as Figure S4 and S5. ^1H NMR (400 MHz, DMSO-d_6) δ 13.62 (s, 1H), 13.36 (s, 1H), 8.27 (d, $J = 1.9$ Hz, 1H), 7.67-7.72 (m, 2H), 7.30-7.46 (m, 3H), 7.04 (d, $J = 8.5$ Hz, 1H), 0.25 (s, 9H); ^{13}C

NMR (400 MHz, DMSO-d6) δ 158.0, 156.6, 150.2, 149.8, 140.0, 134.2, 133.5, 129.3, 127.9, 119.0, 117.3, 114.1, 112.4, 104.5, 91.9, 0.5. The ^1H NMR spectrum exhibits the typical signals for **BTEP**. The peaks of 13.36 ppm and 13.62 ppm attributed to the chemical shifts of -OH at benzene ring and -NH proton in benzimidazole. The peaks range from 7.03 to 8.27 ppm corresponding to the aromatic hydrogens at the benzimidazole and Benzene ring. The single peak at 0.25 ppm was the typical signal of the aromatic hydrogen at the Trimethylsilyl group. The ^{13}C NMR spectrum exhibits 16 peaks, which fully agree with the proposed structure for **BTEP**. The FT-IR spectra shown as Fig. S6, The hydroxyl groups, alkynyl groups, imine groups in the **BTEP** molecule is confirmed by characteristic absorption peaks at 3288 nm, 2152 nm, and 1585 nm.

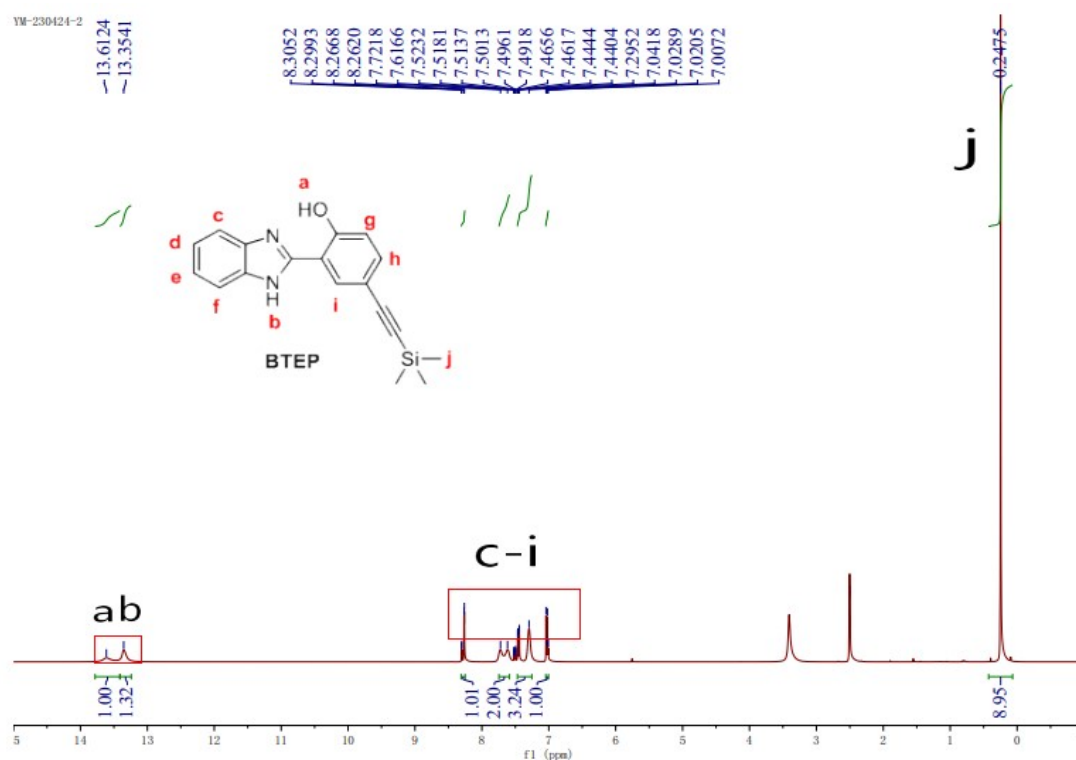


Figure S4. ^1H NMR spectrum (400 MHz, DMSO-d6) of **BTEP**

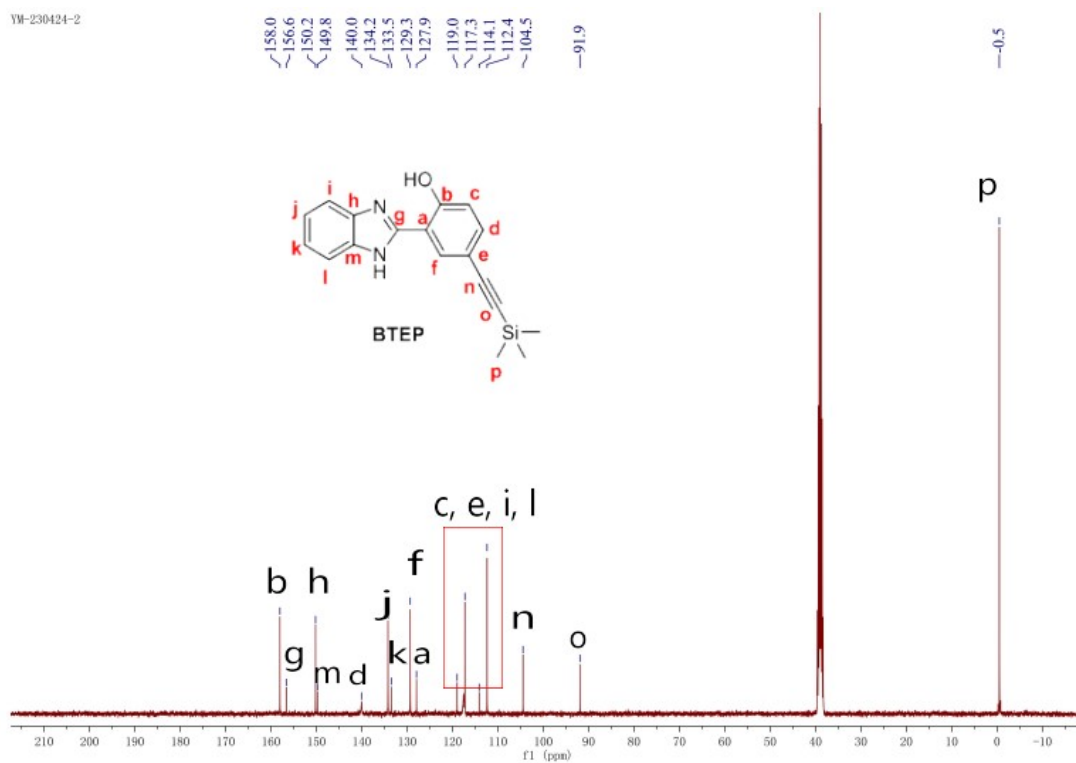


Figure S5. ^{13}C NMR spectrum (100 MHz, DMSO- d_6) of BTEP

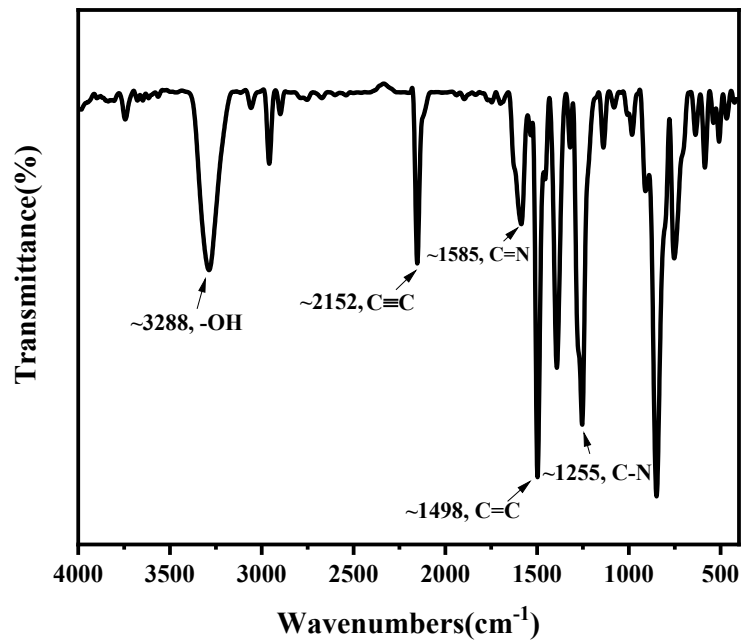


Figure S6. FT-IR spectrum of BTEP

1.4 Detection of BF₃ in different solvents

The stock solutions of **BTEP** (5 mM) and BF₃ were prepared in DCM, ACN, DMF or DMSO solvents. **BTEP** (100 μM) was mixed with BF₃ (200 μM) in according solvents, and then the mixture was incubated at room temperature for 60 s. Emission spectra were measured in the range of 365 nm to 700 nm with an excitation wavelength at 345 nm, and the slit width is 10 nm/20 nm.

1.5 Detection of BF₃ in different incubation time

The stock solutions of **BTEP** (5 mM), BF₃ (5 mM) were prepared in DCM. Various amount of those stock solutions were added into DCM, diluting to the testing solution consist of **BTEP** (100 μM) and BF₃ (200 μM). Then the mixture was incubated at room temperature for different time. Under the same conditions, a detection system without BF₃ was used as the control group. Emission spectra were measured in the range of 365 nm to 700 nm with an excitation wavelength at 345 nm, and the slit width is 10 nm/20 nm.

1.6 Emission titration experiments

The **BTEP** stock solution was added into DCM to a final concentration of 50 μM. A various concentrations of BF₃ (0-100 μM) were then added to DCM containing **BTEP** (50 μM) in a cuvette. Then emission spectra were measured in the range of 365 nm to 700 nm with an excitation wavelength at 345 nm, and the slit width is 10 nm/20 nm.

1.7 Detection of BF₃ with interference substances

5 mM of various common borates and fluorides were prepared in DCM as stock

solutions. Various interferers (50 μ M bis(pinacolato)diboron, boric acid, phenylboronic acid, allyl trifluoroborate potassium, hydrogen fluoride, trifluoroacetic acid, potassium fluoride, tetrabutylammonium fluoride), instead of BF_3 , were added to DCM solution containing **BTEP** (100 μ M), and the mixture was incubated at room temperature for 60 s. Emission spectra were measured in the range of 365 nm to 700 nm with an excitation wavelength at 345 nm, and the slit width is 10 nm/20 nm.

1.8 Detection mechanism experiment

5 mM of **BTEP** was prepared in CDCl_3 as blank testing solution for ^1H NMR, and then recorded on Bruker Avance AV400 spectrometer (Bruker, Billerica, MA, USA). 5 mM of BF_3 in CDCl_3 was added into the blank testing solution, then the mixture was incubated at room temperature for 60 s, and recorded on Bruker Avance AV400 spectrometer .

1.9 Preparation of test strip and naked-eye detection of BF_3 gas

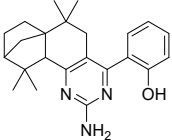
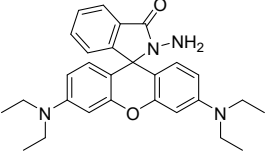
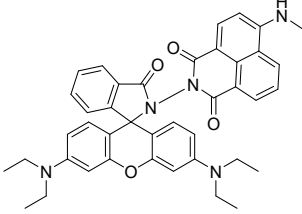
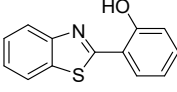
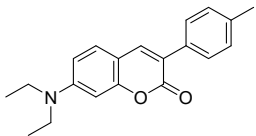
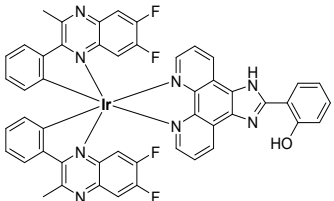
The paper strip was prepared by soaking filter paper (WhatmanTM #.2) with the solution of **BTEP** (5.0%, w/w, DCM). After drying in the vacuum oven, the paper strip was cut into 1.0 \times 4.0 cm rectangle shape. To detect the gaseous BF_3 , prepared paper strip was fastened to the wall of a vial (30 mL). After removing the air in the vials using a high vacuum pump, different concentrations of BF_3 solution were added into the vials avoiding direct contact with the paper strip. Finally, to facilitate vaporization of the BF_3 species, the vials were preheated to 50 $^\circ\text{C}$, and then the detection were proceeded at room temperature.

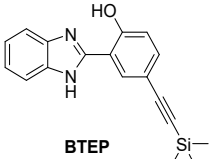
2. COMPARISON OF THE NOVEL FLUORESCENT PROBE WITH OTHER REPORTED PORBES.

The sensitivity data of several fluorescent probes for the detection of BF_3 were

compared with the proposed probe as shown in table S1. It can be seen that the proposed fluorescent probe possesses the lower detection limit, the wider linear range and higher sensitivity compared with the reported probe.

Table S1 Comparison of novel BF₃ probe with other previously reported fluorescent probe.

Entry	Probe	Ex/Em (nm)	Response time (s)	Linear range (μM)	LOD (nM)	Ref.
1		300/428	60	0-10 μM	13.4	S1
2		- /586	< 60	1-9 μM	1.4	S2
3		455/533, 586	< 60	130-200 μM	2.7 × 10 ⁴	S3
4		343/430	< 60	-	500	S4
5		365/408, 464	90	0-80 μM	550	S5
6		280/475, 650	5	0-100 μM	350	S6

7	 <p>BTEP</p>	345/408, 479	60	5-50 μ M	69.5	This work
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3. REFERENCE

- [S1] Z. L. Wang, Y. Zhang, J. Song, Y. Y. Wang, M. X. Li, Y. Q. Yang, X. Xu, H. J. Xu, S. F. Wang. *Sens. Actuators, B*, **2020**, 304, 127083.
- [S2] Y. Z. Wang, Y. Yang, F. Z. Qiu, Y. Feng, X. R. Song, G. L. Zhang, W. S. Liu. *Sens. Actuators, B*, **2018**, 276, 166.
- [S3] Y. M. Liu, J. Y. Zhang, Y. Z. Wang, C. Y. Liu, G. L. Zhang, W. S. Liu. *Sens. Actuators, B*, **2017**, 243, 940.
- [S4] M. G. Choi, S. H. Lee, Y.-U. Jung, J. M. Hong, S.-K. Chang. *Sens. Actuators, B*, **2017**, 251, 713.
- [S5] H. J. Zhao, T. Wu, Y. Sun, L. Duan, Y. Y. Ma. *Chem. J. Chinese U.*, **2021**, 42, 2422.
- [S6] C. K. Lin, J. Wang, K. Yang, J. B. Liu, D.-L. Ma, C.-H. Leung, W. H. Wang. *Spectrochim. Acta. A Mol. Biomol. Spectrosc.*, **2022**, 282, 121658.