 A reductant-resistant ratiometric, colorimetric and far-red fluorescent probe for rapid and ultrasensitive detection of nitroxyl Caiyun Liu,^{a,b}t Yawei Wang,^bt Chengcheng Tang,^b Fang Liu,^b Zhenmin Ma,^b Qiang Zhao,^b Zhongpeng Wang,^b Baocun Zhu ^{b,*} and Xiaoling Zhang ^{a,*} <i>key Laboratory of Cluster Science of Ministry of Education, School of Chemistry, Beijing</i> <i>Institute of Technology, Beijing 100081, China</i> <i>b School of Resources and Environment, University of Jinan, Shandong Provincial</i> <i>Engineering Technology Research Center for Ecological Carbon Sink and Capture</i> Utilization, Jinan 250022, China <i>Corresponding author, Fax: +86-10-88875298; Tel.: +86-10-88875298</i> <i>E-mail address: lcyzbc@163.com (B. Zhu); zhangxl@bit.edu.cn</i> These authors contributed equally to the present work. Contents I. Synthesis of reference compound R-TCF J. The effects of pH on the fluorescence intensity of probe HNO-TCF J. The fluorescence spectrometry of reference compound R-TCF 	1	Supporting Information
4 and ultrasensitive detection of nitroxyl 5 Caiyun Liu, *b [±] Yawei Wang, ^b t Chengcheng Tang, ^b Fang Liu, ^b Zhenmin Ma, ^b Qiang Zhao, ^b 6 Zhongpeng Wang, ^b Baocun Zhu ^{b,*} and Xiaoling Zhang ^{a,*} 7 * 8 * Key Laboratory of Cluster Science of Ministry of Education, School of Chemistry, Beijing 9 Institute of Technology, Beijing 100081, China 10 ^b School of Resources and Environment, University of Jinan, Shandong Provincial 11 Engineering Technology Research Center for Ecological Carbon Sink and Capture 12 Utilization, Jinan 250022, China 13 *Corresponding author. Fax: +86-10-88875298; Tel.: +86-10-88875298 14 E-mail address: lcyzbc@163.com (B. Zhu); zhangxl@bit.edu.cn 15 *These authors contributed equally to the present work. 16	2	
 Caiyun Liu, ^{a,b‡} Yawei Wang,^{b‡} Chengcheng Tang,^b Fang Liu,^b Zhenmin Ma,^b Qiang Zhao,^b Zhongpeng Wang,^b Baocun Zhu ^{b,*} and Xiaoling Zhang ^{a,*} ^a Key Laboratory of Cluster Science of Ministry of Education, School of Chemistry, Beijing Institute of Technology, Beijing 100081, China ^b School of Resources and Environment, University of Jinan, Shandong Provincial Engineering Technology Research Center for Ecological Carbon Sink and Capture Utilization, Jinan 250022, China [*]Corresponding author. Fax: +86-10-88875298; Tel.: +86-10-88875298 E-mail address: lcyzbc@163.com (B. Zhu); zhangxl@bit.edu.cn [*]These authors contributed equally to the present work. 1 Contents 1. Synthesis of reference compound R-TCF 2. The effects of pH on the fluorescence intensity of probe HNO-TCF 3. The fluorescence spectrometry of reference compound R-TCF 4. 'H-NMR, ¹³C-NMR and HRMS spectra of probe HNO-TCF 	3	A reductant-resistant ratiometric, colorimetric and far-red fluorescent probe for rapid
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 12 Utilization, Jinan 250022, China 13 *Corresponding author. Fax: +86-10-88875298; Tel.: +86-10-88875298 14 E-mail address: lcyzbc@163.com (B. Zhu); zhangxl@bit.edu.cn 15 [‡] These authors contributed equally to the present work. 16 17 18 Contents 19 1. Synthesis of reference compound R-TCF 20 2. The effects of pH on the fluorescence intensity of probe HNO-TCF 21 3. The fluorescence spectrometry of reference compound R-TCF 22 4. ¹H-NMR, ¹³C-NMR and HRMS spectra of probe HNO-TCF 	10	^b School of Resources and Environment, University of Jinan, Shandong Provincial
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 16 17 18 Contents 19 1. Synthesis of reference compound R-TCF 20 2. The effects of pH on the fluorescence intensity of probe HNO-TCF 21 3. The fluorescence spectrometry of reference compound R-TCF 22 4. ¹H-NMR, ¹³C-NMR and HRMS spectra of probe HNO-TCF 	14	E-mail address: lcyzbc@163.com (B. Zhu); zhangxl@bit.edu.cn
 17 18 Contents 1. Synthesis of reference compound R-TCF 2. The effects of pH on the fluorescence intensity of probe HNO-TCF 3. The fluorescence spectrometry of reference compound R-TCF 2. 4. ¹H-NMR, ¹³C-NMR and HRMS spectra of probe HNO-TCF 	15	[‡] These authors contributed equally to the present work.
 Contents Synthesis of reference compound R-TCF The effects of pH on the fluorescence intensity of probe HNO-TCF The fluorescence spectrometry of reference compound R-TCF 4. ¹H-NMR, ¹³C-NMR and HRMS spectra of probe HNO-TCF 	16	
 1. Synthesis of reference compound R-TCF 2. The effects of pH on the fluorescence intensity of probe HNO-TCF 3. The fluorescence spectrometry of reference compound R-TCF 4. ¹H-NMR, ¹³C-NMR and HRMS spectra of probe HNO-TCF 	17	
 20 2. The effects of pH on the fluorescence intensity of probe HNO-TCF 21 3. The fluorescence spectrometry of reference compound R-TCF 22 4. ¹H-NMR, ¹³C-NMR and HRMS spectra of probe HNO-TCF 	18	Contents
 3. The fluorescence spectrometry of reference compound R-TCF 4. ¹H-NMR, ¹³C-NMR and HRMS spectra of probe HNO-TCF 	19	1. Synthesis of reference compound R-TCF
22 4. ¹ H-NMR, ¹³ C-NMR and HRMS spectra of probe HNO-TCF	20	2. The effects of pH on the fluorescence intensity of probe HNO-TCF
	21	3. The fluorescence spectrometry of reference compound R-TCF
23	22	4. ¹ H-NMR, ¹³ C-NMR and HRMS spectra of probe HNO-TCF
	23	

24 1. Synthesis of reference compound R-TCF



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Scheme S1 The synthesis of R-TCF

A mixture of 1-(3-cyano-2-dicyanomethylen-5, 5-dimethyl-2, 5-dihydrofuran-4-yl)-2-27 (4-hydroxylphenyl) ethane (compound 2, 303 mg, 1 mmol), benzoic acid (366 mg, 3 mmol), 28 4-dimethylaminopyridine (DMAP, 244 mg, 2 mmol) and dicyclohexylcarbodiimide (DCC, 29 826 mg, 4 mmol) in CH₂Cl₂ (30 mL) was stirred at 45 °C for 8 hours. After cooled to room 30 temperature, the reaction mixture was purified by silica column chromatography (CH_2Cl_2 as 31 eluent) in order to get pure reference compound **R-TCF**. ¹H-NMR (400 MHz, DMSO- d_6) δ 32 $(*10^{-6})$: 1.82(s, 6H), 7.27(d, J = 16 Hz, 1H), 7.49(d, J = 8 Hz, 2H), 7.64(t, J = 8 Hz, 33 2H), 7.79(t, J = 8 Hz, 1H), 7.97(d, J = 20 Hz, 1H), 8.06(d, J = 8 Hz, 2H), 8.17(d, J = 100)34 8 Hz, 2H). ¹³C-NMR (100 MHz, DMSO-*d*₆) δ (*10⁻⁶): 25.55, 54.93, 99.98, 100.18, 111.29, 35 112.30, 113.14, 116.06, 123.40, 129.08, 129.52, 130.38, 131.37, 132.74, 134.76, 146.67, 36 153.90, 164.75, 175.55, 177.60. ESI-MS (positive) calcd for C₂₅H₁₇N₃O₃Na [M+Na]⁺ 430.1, 37 found 430.1. 38

39 2. The effects of pH on the fluorescence intensity of probe HNO-TCF

The pH effects on the fluorescence intensity of probe **HNO-TCF** and compound **2** (5 41 μ M) in a mixture of ethanol and water (5:5, v/v) solution containing 5 mM PBS were 42 examined.



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Fig. S1 The effects of pH on the fluorescence intensity of probe **HNO-TCF** and compound **2** (5 μ M) a mixture of ethanol and water (5:5, ν/ν) solution containing 5 mM PBS. All data represent the fluorescence intensity at 614 nm. Excitation wavelength = 560 nm, excitation and emission slit widths = 10 nm and 10 nm.

48 3. The fluorescence spectrometry of reference compound R-TCF

To eliminate concerns about the effect of the HNO-TCF oxide on the fluorescence 49 detection, the fluorescence spectrometry of R-TCF (5 μ M) have been investigated. As shown 50 in Fig. S2, Only negligible fluorescence of R-TCF, similar to the fluorescence of HNO-TCF, 51 was observed, which is probable due to the inhibition of effective internal charge transfer 52 (ICT) resulted from the protection of hydroxyl (J. Am. Chem. Soc., 2012, 134, 13510). 53 To understand the mechanism of HNO-TCF in sensing HNO, the reference experiment 54 about the effect of HNO on the fluorescence spectrometry of R-TCF (5 μ M) was also carried 55 out. The result exhibited that addition of AS (100 μ M) did not result in the distinguishable 56 fluorescence enhancement of R-TCF, implying that the reaction of HNO-TCF with HNO 57

58 was attributed to the 2-(diphenylphosphino)benzoate recognition moiety.



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60 Fig. S2 The fluorescence spectra of R-TCF (5 μ M) in the absence and presence of AS (100 μ M) in a

61 mixture of ethanol and water (5:5, v/v) solution containing 5 mM PBS (pH 7.4) at 25 °C. Excitation

62 wavelength = 560 nm, excitation and emission slit widths = 10 nm and 10 nm.

63 4. ¹H-NMR, ¹³C-NMR and HRMS spectra of probe HNO-TCF

64 ¹H-NMR probe HNO-TCF





70 HRMS spectra of probe HNO-TCF

