

Supporting Information

A reductant-resistant ratiometric, colorimetric and far-red fluorescent probe for rapid and ultrasensitive detection of nitroxyl

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Contents

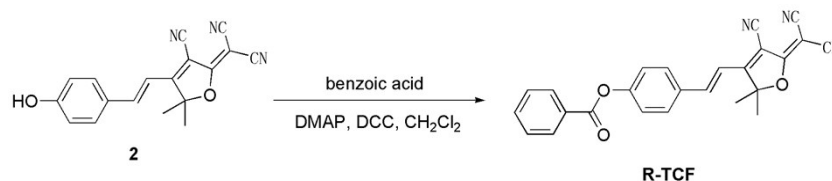
1. Synthesis of reference compound R-TCF

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

3. The fluorescence spectrometry of reference compound R-TCF

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

24 1. Synthesis of reference compound R-TCF

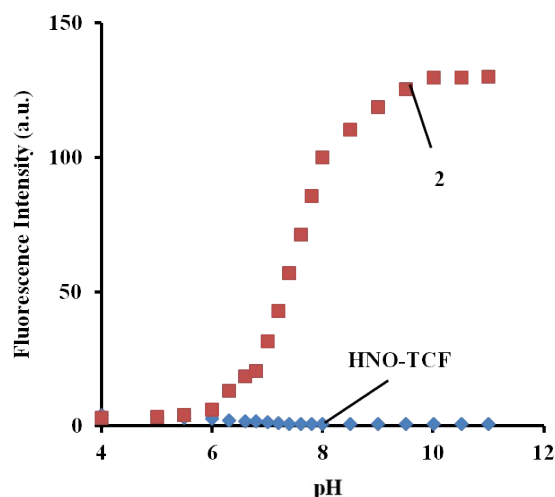


26 **Scheme S1** The synthesis of **R-TCF**

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

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

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

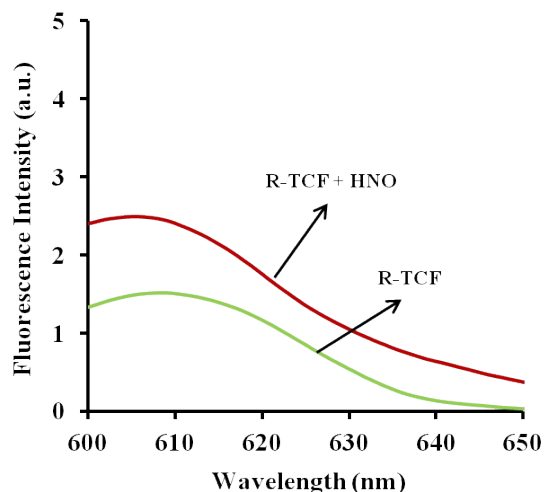


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 44 **Fig. S1** The effects of pH on the fluorescence intensity of probe **HNO-TCF** and compound **2** ($5\ \mu\text{M}$) a
 45 mixture of ethanol and water (5:5, v/v) solution containing 5 mM PBS. All data represent the fluorescence
 46 intensity at 614 nm. Excitation wavelength = 560 nm, excitation and emission slit widths = 10 nm and 10
 47 nm.

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

49 To eliminate concerns about the effect of the **HNO-TCF** oxide on the fluorescence
 50 detection, the fluorescence spectrometry of **R-TCF** ($5\ \mu\text{M}$) have been investigated. As shown
 51 in Fig. S2, Only negligible fluorescence of **R-TCF**, similar to the fluorescence of **HNO-TCF**,
 52 was observed, which is probable due to the inhibition of effective internal charge transfer
 53 (ICT) resulted from the protection of hydroxyl (*J. Am. Chem. Soc.*, 2012, 134, 13510).

54 To understand the mechanism of **HNO-TCF** in sensing HNO, the reference experiment
 55 about the effect of HNO on the fluorescence spectrometry of **R-TCF** ($5\ \mu\text{M}$) was also carried
 56 out. The result exhibited that addition of AS ($100\ \mu\text{M}$) did not result in the distinguishable
 57 fluorescence enhancement of **R-TCF**, implying that the reaction of **HNO-TCF** with HNO
 58 was attributed to the 2-(diphenylphosphino)benzoate recognition moiety.

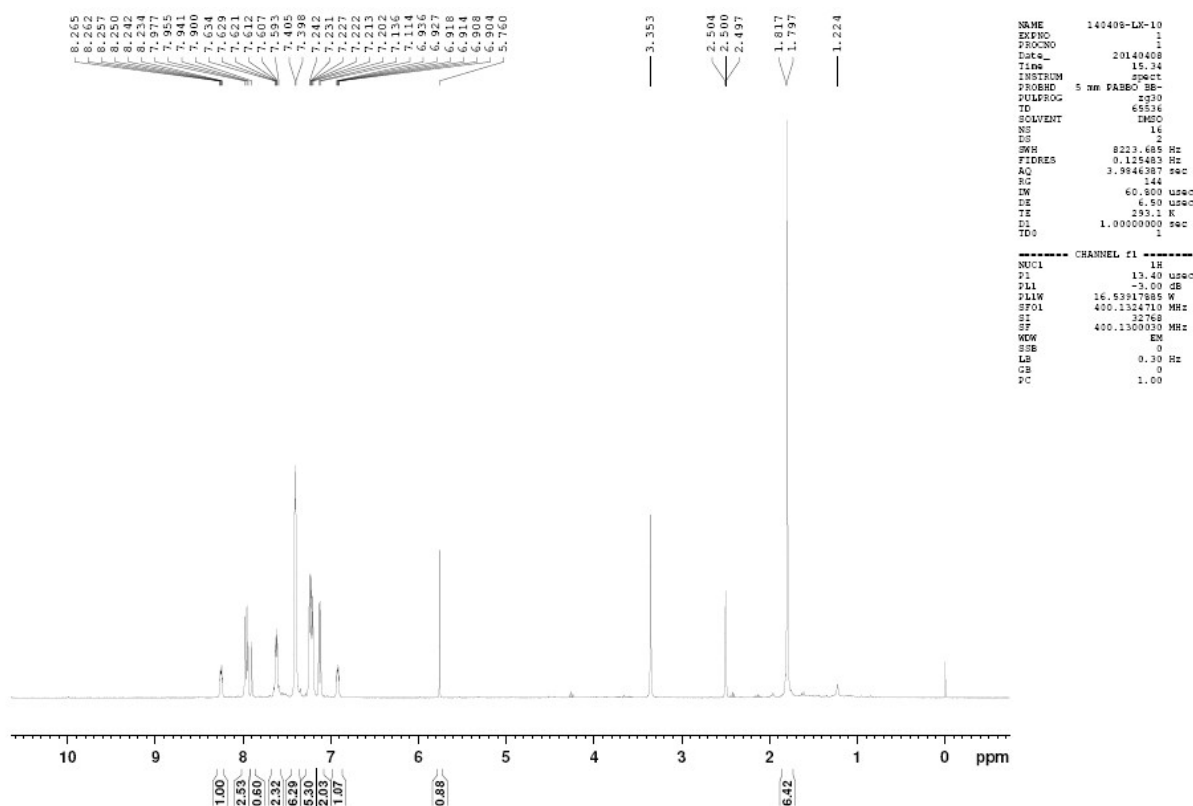


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60 **Fig. S2** The fluorescence spectra of **R-TCF** (5 μ M) in the absence and presence of **AS** (100 μ M) in a
 61 mixture of ethanol and water (5:5, v/v) solution containing 5 mM PBS (pH 7.4) at 25 $^{\circ}$ C. Excitation
 62 wavelength = 560 nm, excitation and emission slit widths = 10 nm and 10 nm.

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

64 ^1H -NMR probe HNO-TCF



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