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#### 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 CH<sub>2</sub>Cl<sub>2</sub> (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**. <sup>1</sup>H-NMR (400 MHz, DMSO- $d_6$ )  $\delta$ 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). <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ (\*10<sup>-6</sup>): 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 C<sub>25</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 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  $\mu$ M) in a mixture of ethanol and water (5:5, v/v) solution containing 5 mM PBS were 42 examined.



#### 43

**Fig. S1** The effects of pH on the fluorescence intensity of probe **HNO-TCF** and compound **2** (5  $\mu$ M) a mixture of ethanol and water (5:5,  $\nu/\nu$ ) 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  $\mu$ 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  $\mu$ M) was also carried 55 out. The result exhibited that addition of AS (100  $\mu$ 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.



59

60 Fig. S2 The fluorescence spectra of R-TCF (5  $\mu$ M) in the absence and presence of AS (100  $\mu$ 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. <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and HRMS spectra of probe HNO-TCF

## 64 <sup>1</sup>H-NMR probe HNO-TCF





## 70 HRMS spectra of probe HNO-TCF

