

A pyridomethene-BF₂ complex-based chemosensor for detection of hydrazine

Yan-Duo Lin and Tahsin J. Chow^{*a}

^a Institute of Chemistry, Academia Sinica, Taipei 115 Taiwan

tjchow@chem.sinica.edu.tw

Supporting Information

Contents:

S1	Table of Contents
S2, S3, S4	¹ H, ¹³ C, and ¹⁹ F NMR spectra of 3 .
S5, S6, S7	¹ H, ¹³ C, and ¹⁹ F NMR spectra of PBF₂ .
S8	Figure S7. Time-dependent absorption spectra of sensor PBF₂ (1 x 10 ⁻⁵ M) upon the addition of hydrazine (10 equiv) in a mixture of acetate buffer (pH 4.0, 10 mM) and DMSO (1/9, v/v). The arrows indicate the change of incubation time 0 to 8 mins.
S9	Figure S8. Normalized absorption spectra of PBF₂ in cyclohexane, toluene, THF, ethyl acetate, dichloromethane, and acetonitrile.
S10	Figure S9. (a) Absorption and (b) fluorescence spectra of PBF₂ (1 x 10 ⁻⁵ M in a mixture of acetate buffer (pH 4.0, 10 mM) and DMSO (1/9, v/v)) in the presence of hydrazine and ions (F ⁻ , Cl ⁻ , Br ⁻ , I ⁻ , CN ⁻ , ClO ₄ ⁻ , H ₂ PO ₄ ⁻ , HSO ₄ ⁻ , NO ₃ ⁻ , CH ₃ CO ₂ ⁻ , Li ⁺ , Na ⁺ , K ⁺ , Cs ⁺ , Ag ⁺ , Ba ²⁺ , Ca ²⁺ , Mg ²⁺ , Co ²⁺ , Cu ²⁺ , Pb ²⁺ , Zn ²⁺ , Y ³⁺).
S11	Figure S10. The fluorescence intensity of sensor PBF₂ (1 x 10 ⁻⁵ M) incubated with hydrazine (2 x 10 ⁻⁴ M) for 0-8 min.
S12	Figure S11. The simulated absorption spectra of sensor PBF₂ (black line) and PBF₂-NH₂ (red line).
S13	Figure S12. IR spectra of probe PBF₂ (upper line), PBF₂ upon addition of hydrazine (bottom line).
S14	Figure S13. ¹ H NMR spectra for a continuous change of PBF₂ to PBF₂-NH₂ .
S15	Figures S14 and S15. The absorption and emission spectra of PBF₂ upon the addition of n-propylamine.
S16	Figure S16. Changes of spectral intensity at different pH.

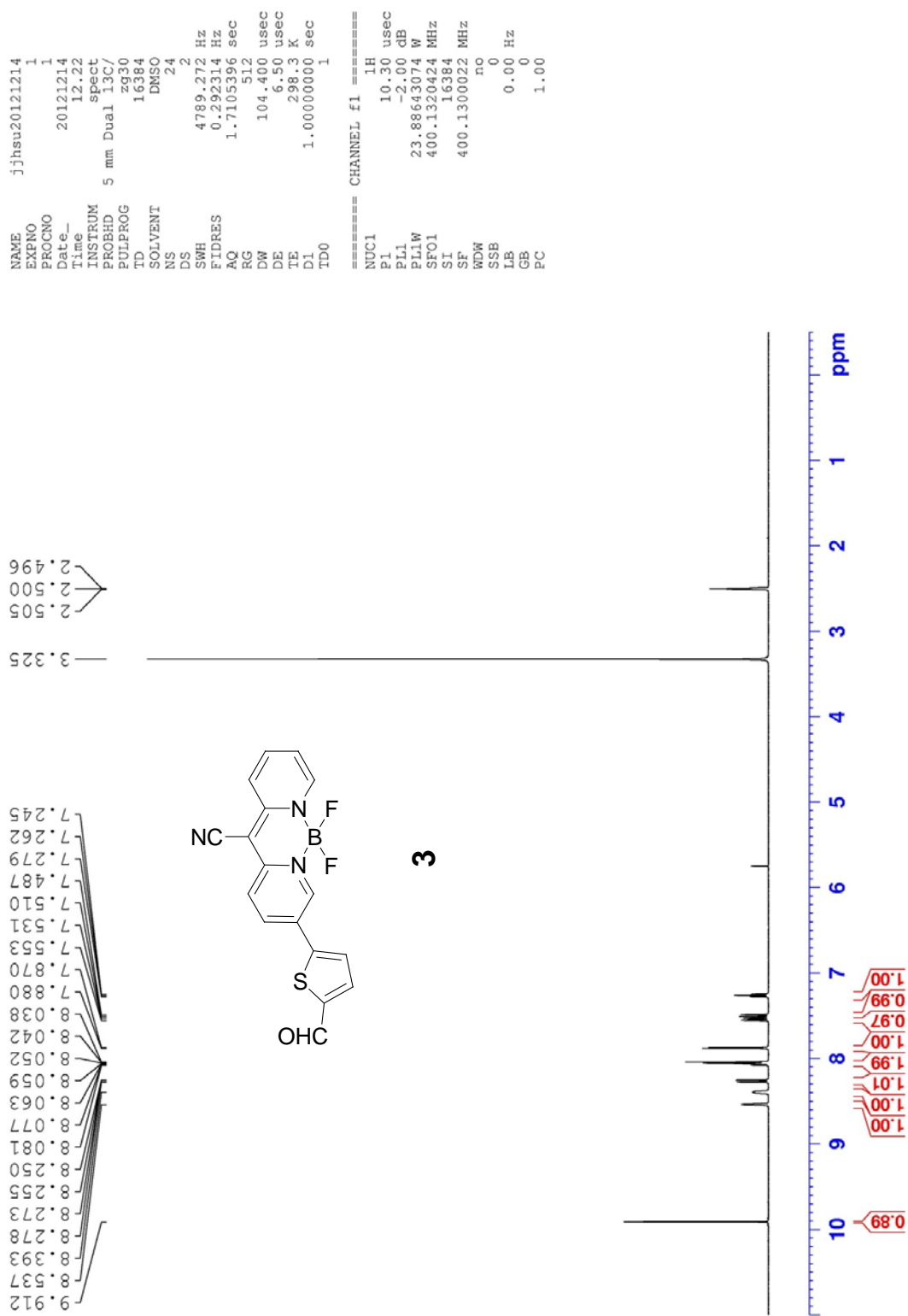


Figure S1. ^1H NMR spectrum of **3**

```
NAME jjhsu20121214
EXPNO 2
PROCNO 1
Date_ 20121214
Time_ 12.26
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgpg30
TD 32768
SOLVENT DMSO
NS 2373
DS 8
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 0.6832628 sec
RG 9195.2
DW 20.850 usec
DE 6.50 usec
TE 298.5 K
D1 3.0000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 6.00 usec
PL1 -1.00 dB
PL1W 47.43416595 W
SF01 100.6228293 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 12.00 dB
PL2W 23.88643074 W
PL3W 0.38739258 W
SF02 400.1518764 MHz
SI 32768
SF 100.6128193 MHz
EM
WDW 0
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
```

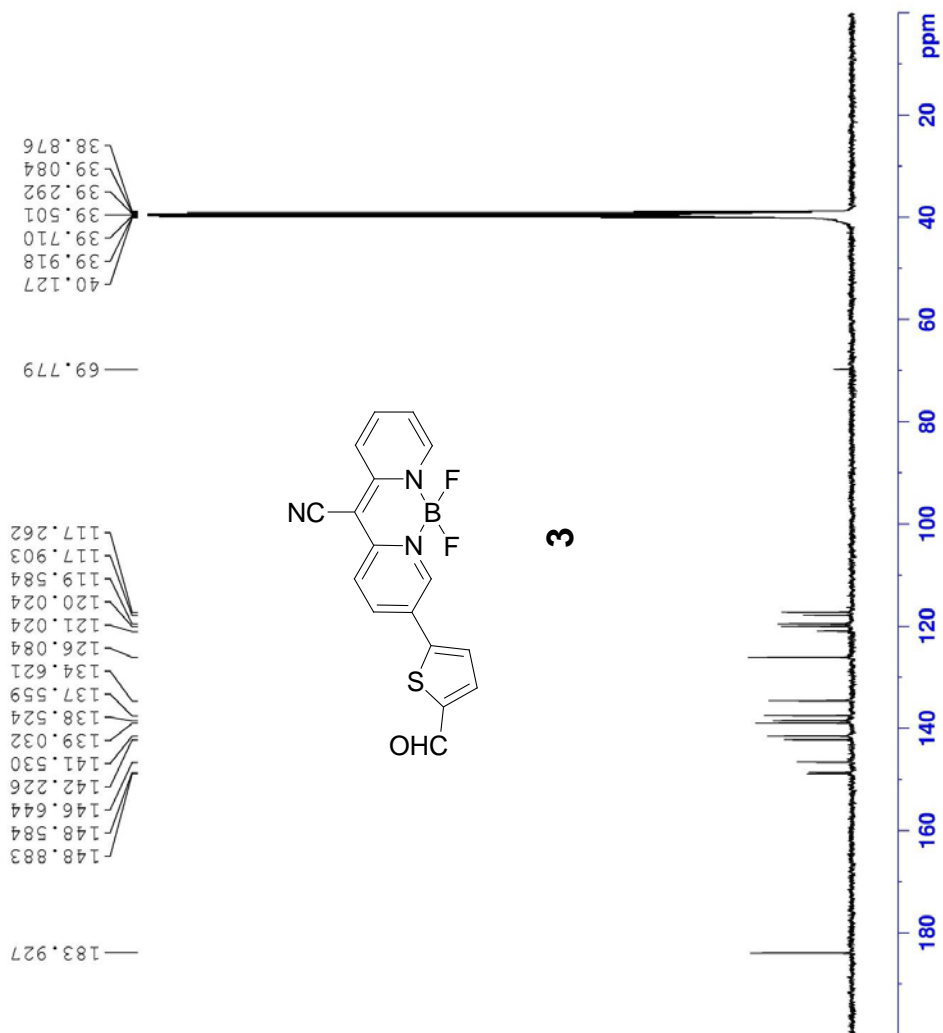


Figure S2. ^{13}C NMR spectrum of **3**

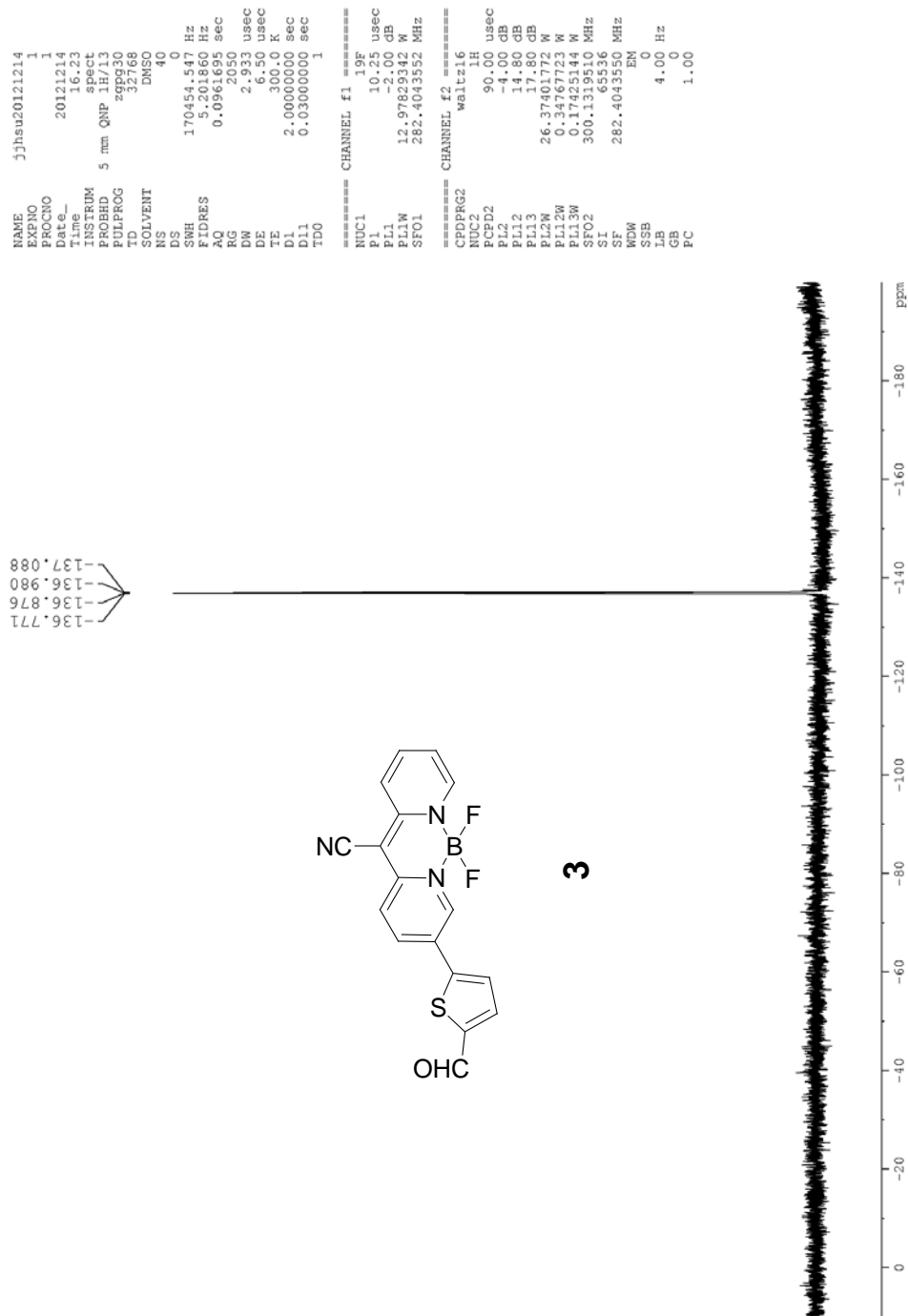


Figure S3. ^{19}F NMR spectrum of **3**

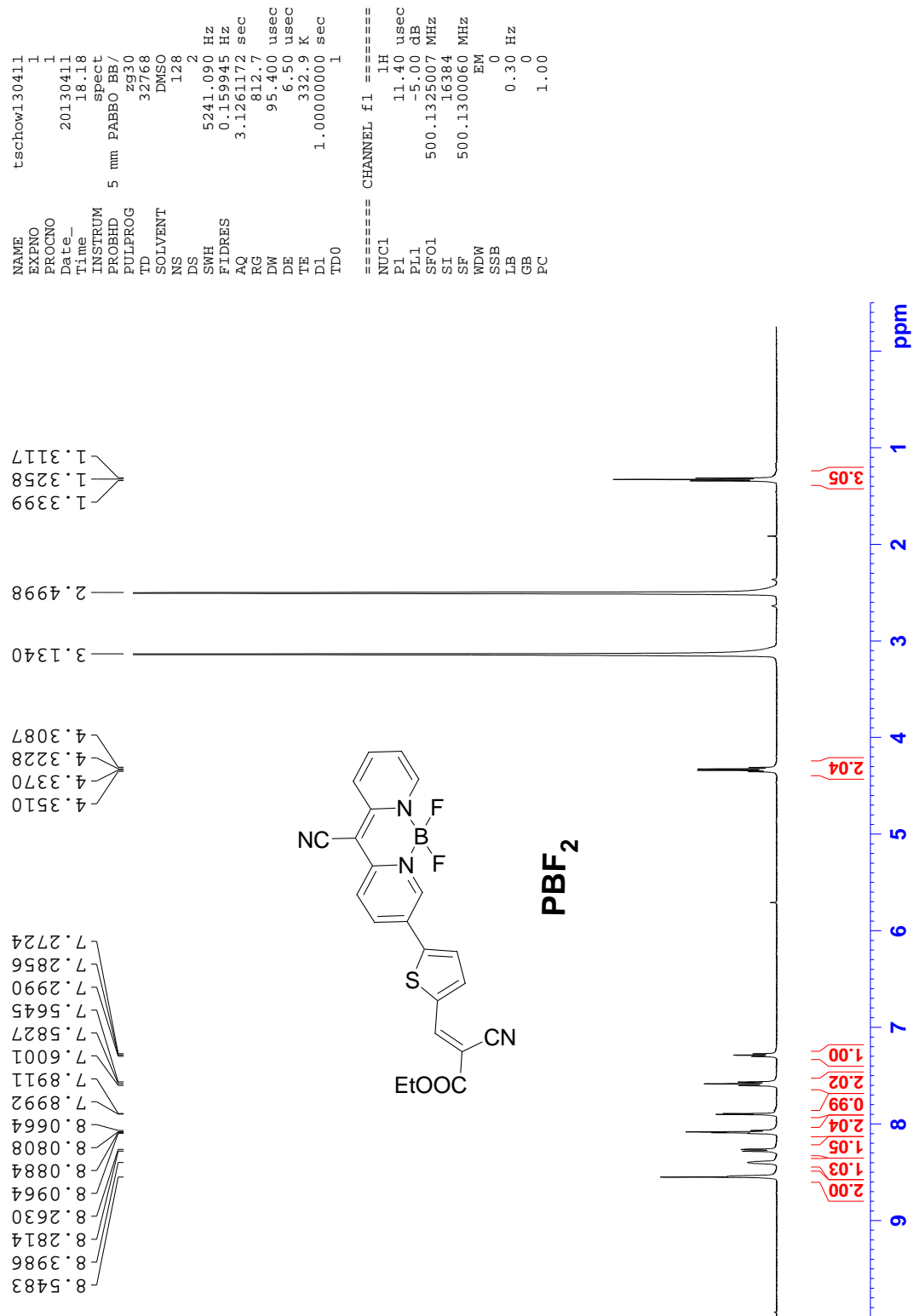


Figure S4. ¹H NMR spectrum of PBF₂

```

NAME          tschow130411
EXPNO         2
PROCNO        1
Date_         20130412
Time         9.43
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zgpg30
TD            32768
SOLVENT       CDCl3
NS            15282
DS            2
SWH           28901.734 Hz
FIDRES       0.882011 Hz
AQ           0.5669364 sec
RG           130004
DE           17.300 usec
TE           6.50 usec
D1           333.0 K
d11          3.00000000 sec
TD0          0.03000000 sec
===== CHANNEL f1 =====
NUC1          13C
P0            4.00 usec
PL1           3.00 dB
SFO1         125.7716224 MHz
===== CHANNEL f2 =====
CPDPRG2      waltz16
NUC2          1H
PCPD2        90.00 usec
PL2          -5.00 dB
PL12         14.60 dB
SFO2         500.1320000 MHz
SI           32768
SF           125.7578899 MHz
WDW           EM
SSB           0
LB           2.00 Hz
GB           0
PC           1.00
    
```

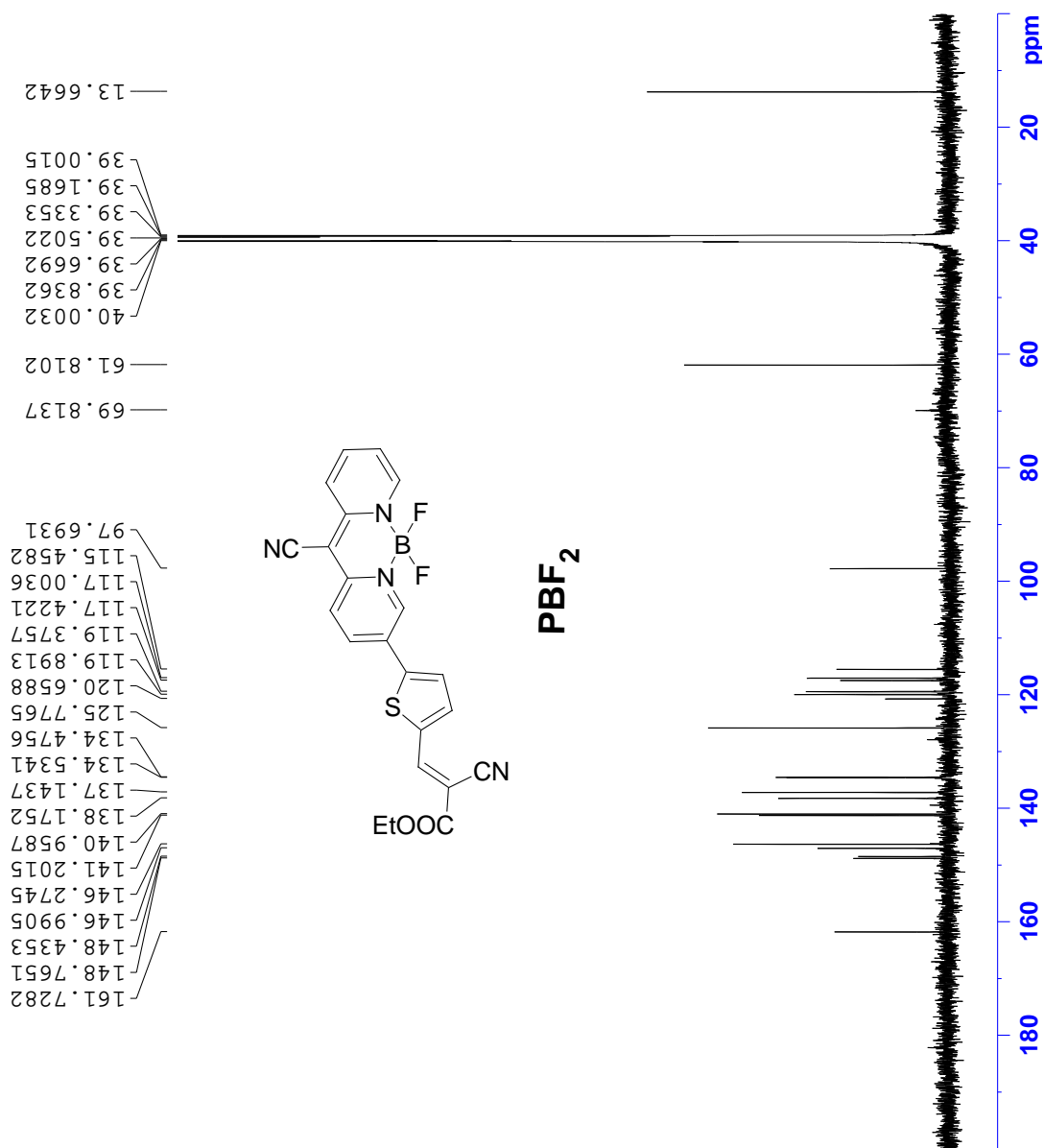


Figure S5. ¹³C NMR spectrum of PBF₂

```
tschow130411
NAME
EXPNO 3
PROCNO 1
Date_ 20130411
Time 18.03
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 131072
SOLVENT CDC13
NS 32
DS 2
SWH 46948.355 Hz
FIDRES 0.358188 Hz
AQ 1.3959668 sec
RG 2048
DE 10.650 usec
TE 333.2 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 19F
P1 13.60 usec
PL1 -5.00 dB
SFO1 470.5264790 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -5.00 dB
PL12 14.60 dB
SFO2 500.1320000 MHz
SI 65536
SF 470.5923620 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
```

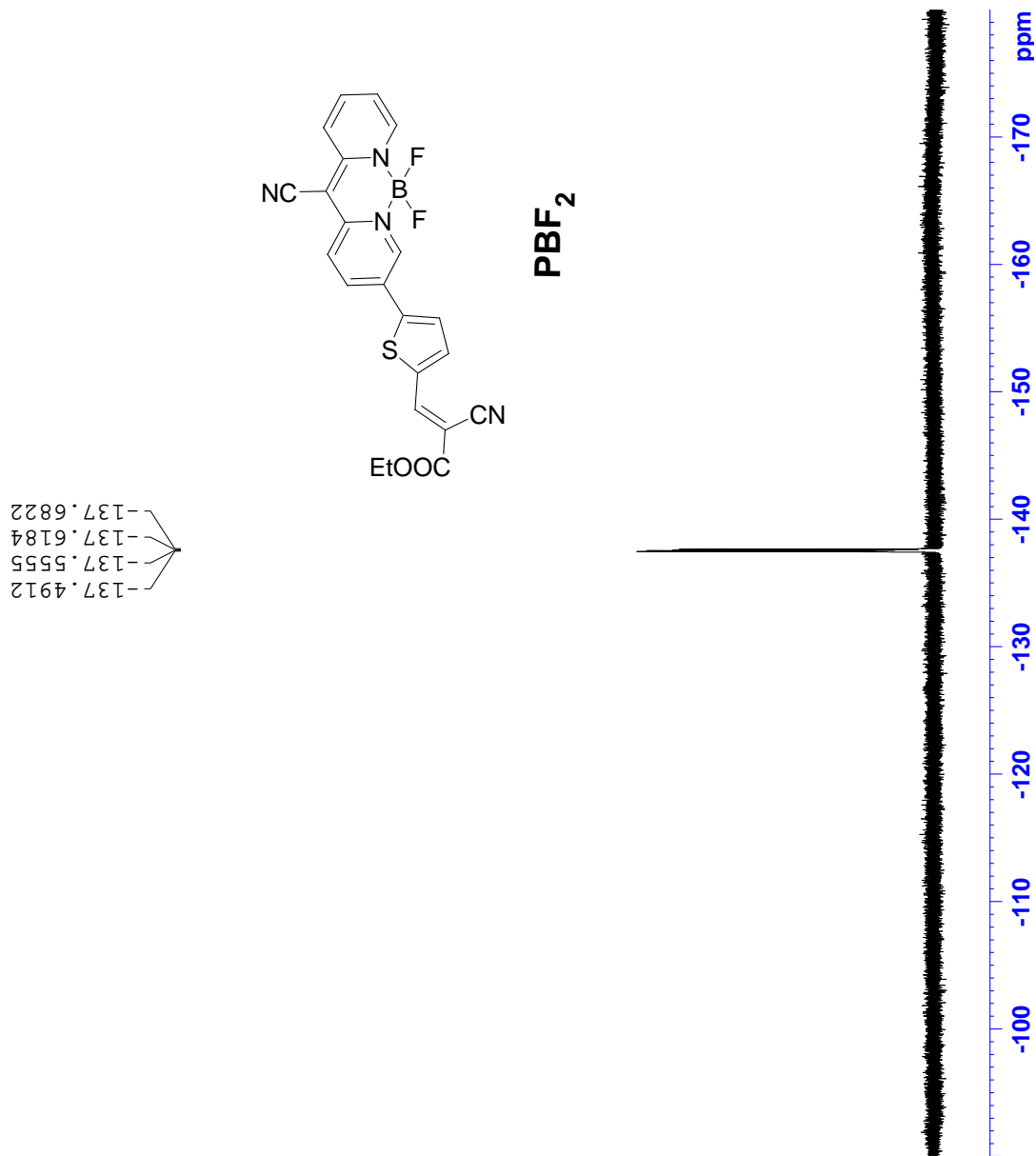


Figure S6. ¹⁹F NMR spectrum of PBF₂

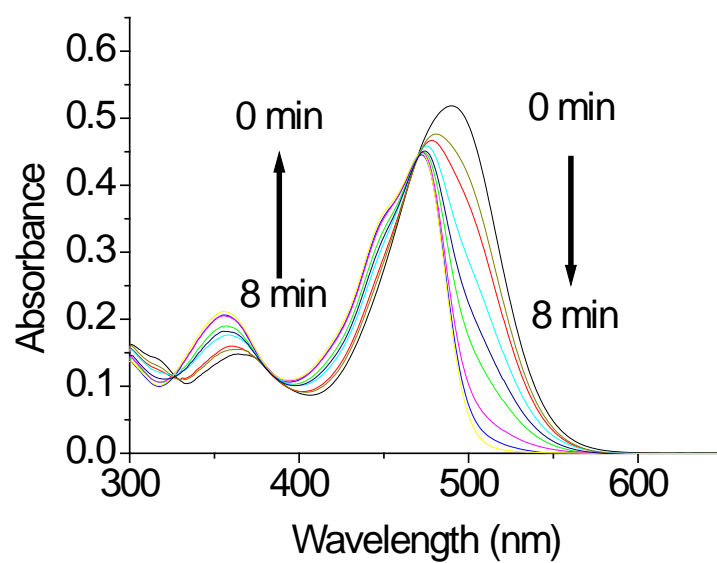


Figure S7. Time-dependent absorption spectra of sensor PBF_2 ($1 \times 10^{-5} \text{ M}$) upon the addition of hydrazine (10 equiv) in a mixture of acetate buffer (pH 4.0, 10 mM) and DMSO (1/9, v/v). The arrows indicate the change of incubation time 0 to 8 min.

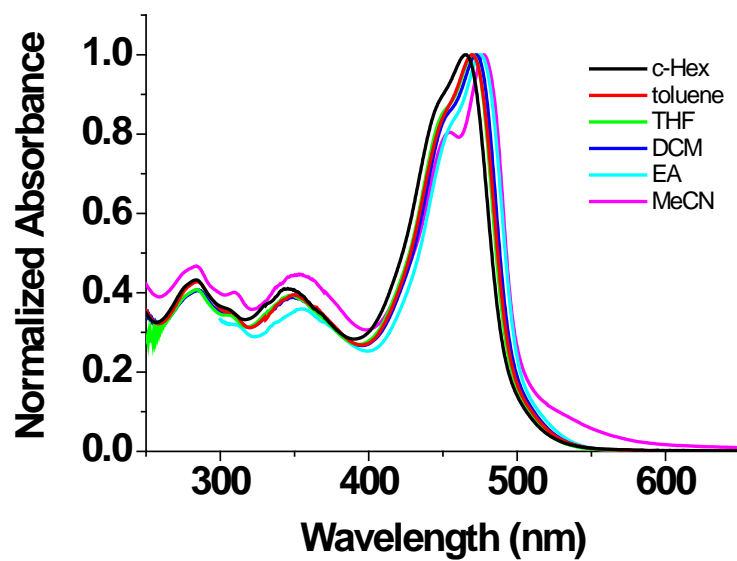


Figure S8. Normalized absorption spectra of **PBF₂** in cyclohexane, toluene, THF, ethyl acetate, dichloromethane, and acetonitrile.

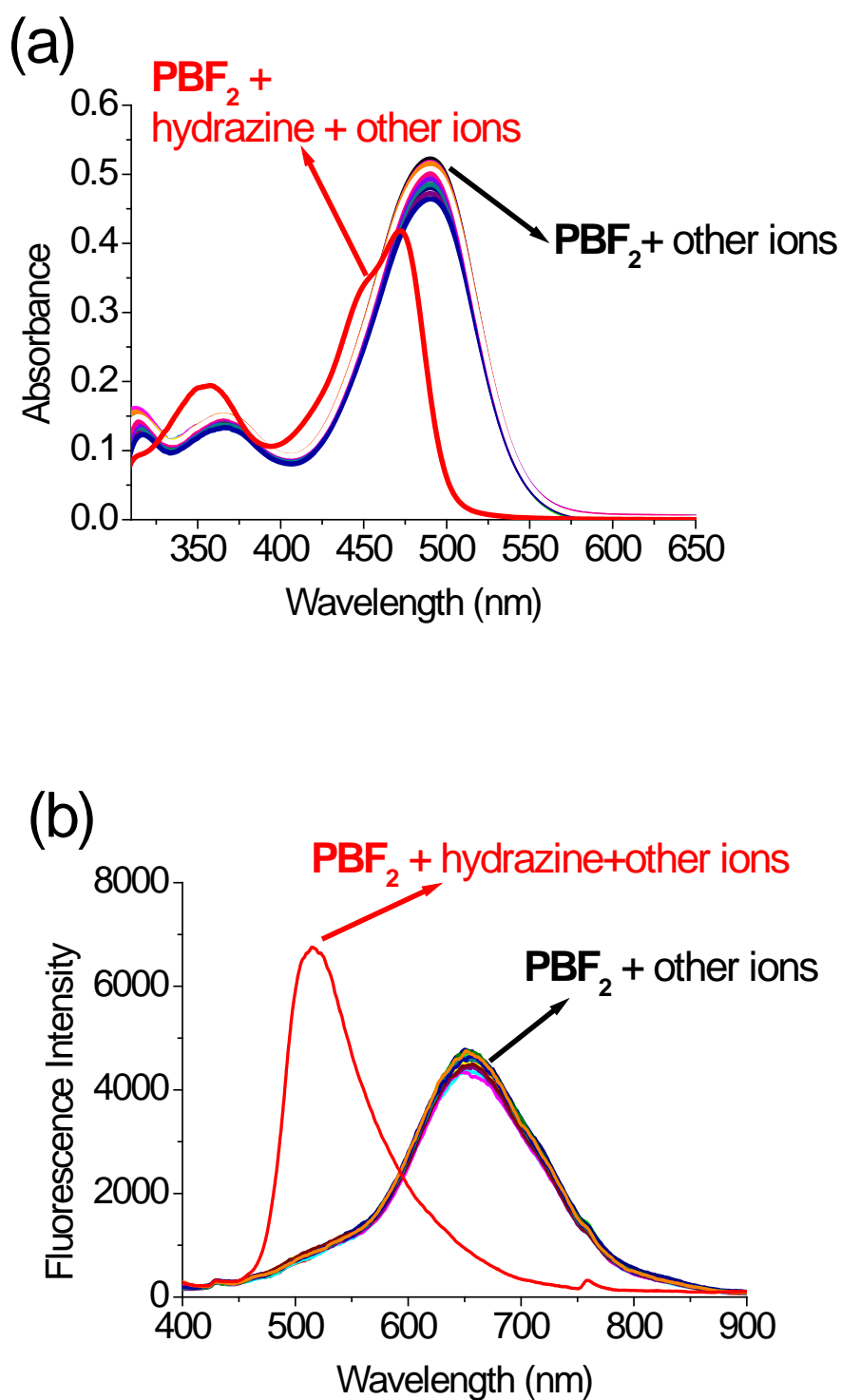


Figure S9. (a) Absorption and (b) fluorescence spectra of **PBF₂** (1×10^{-5} M in a mixture of acetate buffer (pH 4.0, 10 mM) and DMSO (1/9, v/v)) in the presence of hydrazine and ions (F^{-} , Cl^{-} , Br^{-} , I^{-} , CN^{-} , ClO_4^{-} , $H_2PO_4^{-}$, HSO_4^{-} , NO_3^{-} , $CH_3CO_2^{-}$, Li^{+} , Na^{+} , K^{+} , Cs^{+} , Ag^{+} , Ba^{2+} , Ca^{2+} , Mg^{2+} , Co^{2+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Y^{3+}).

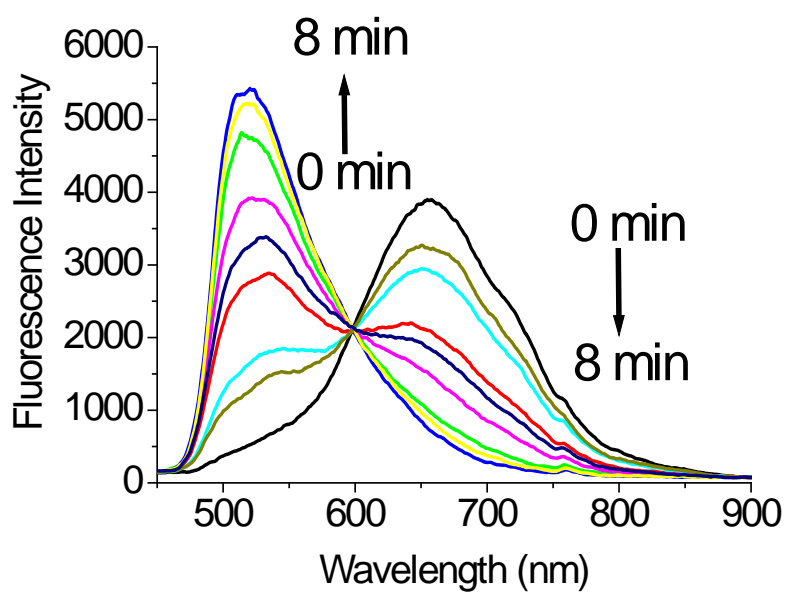


Figure S10. The fluorescence intensity of sensor **PBF₂** (1×10^{-5} M) incubated with hydrazine (2×10^{-4} M) for 0-8 min.

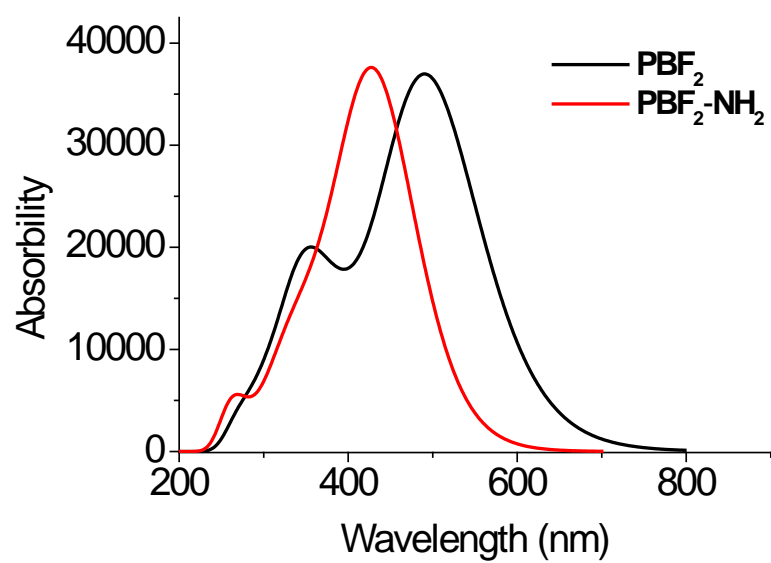


Figure. S11 The simulated absorption spectra of sensor PBF_2 (black line) and $\text{PBF}_2\text{-NH}_2$ (red line).

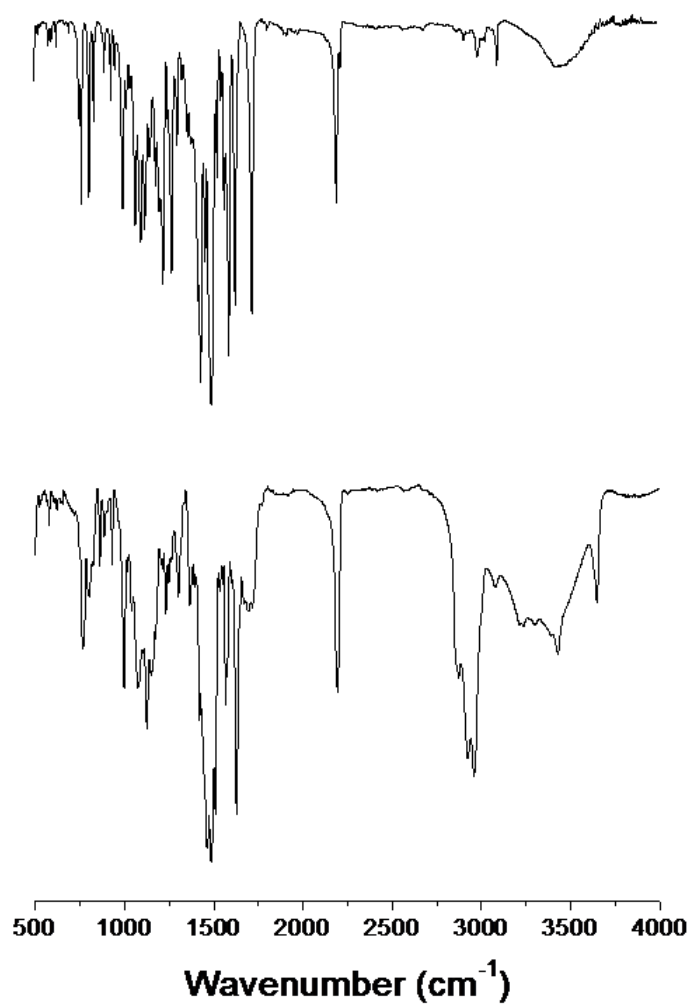


Figure S12. IR spectra of probe **PBF**₂ (upper line), and **PBF**₂ upon addition of hydrazine (bottom line).

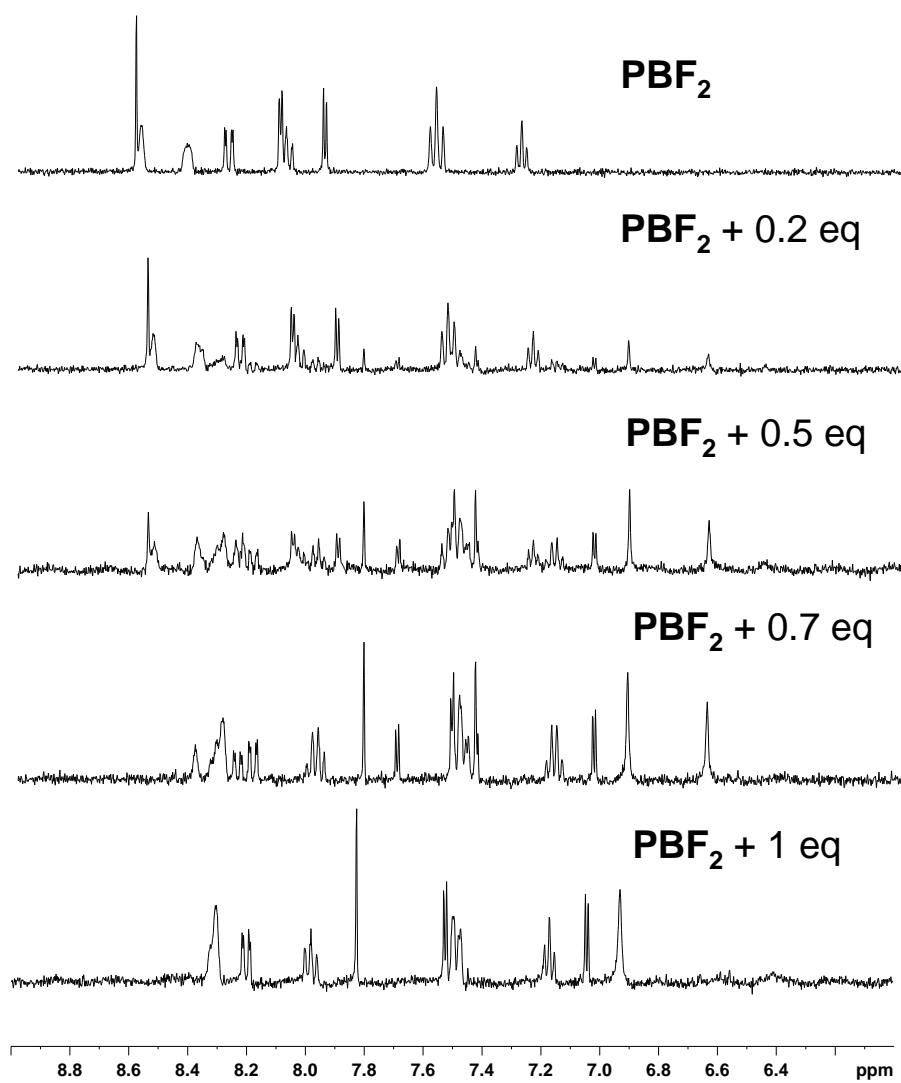


Figure S13. ^1H NMR spectra for a continuous change of PBF_2 to $\text{PBF}_2\text{-NH}_2$.

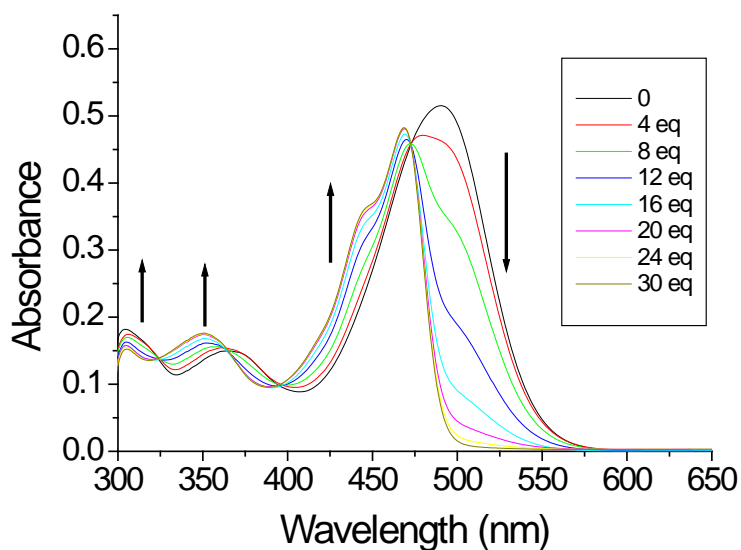


Figure S14. Change of absorption spectrum of **PBF₂** (1×10^{-5} M) upon the addition of *n*-propylamine (0~30 equiv at 4.0 equiv interval) in a mixed solvent of an acetate buffer (pH 4.0, 10 mM) and DMSO (1/9, v/v).

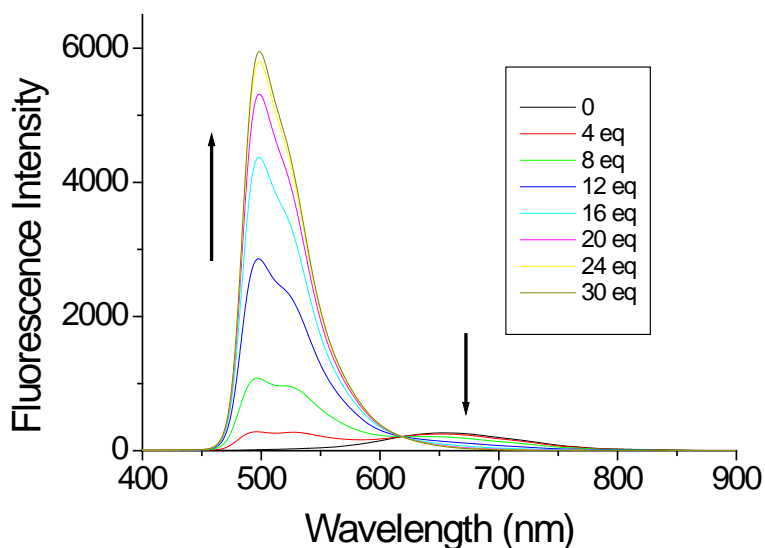


Figure S15. Fluorescence titration spectra of **PBF₂** (1×10^{-5} M in a mixture of acetate buffer (pH 4.0, 10 mM) and DMSO (1/9, v/v)) solution with different concentrations of *n*-propylamine (0~30 equiv at 4.0 equiv interval).

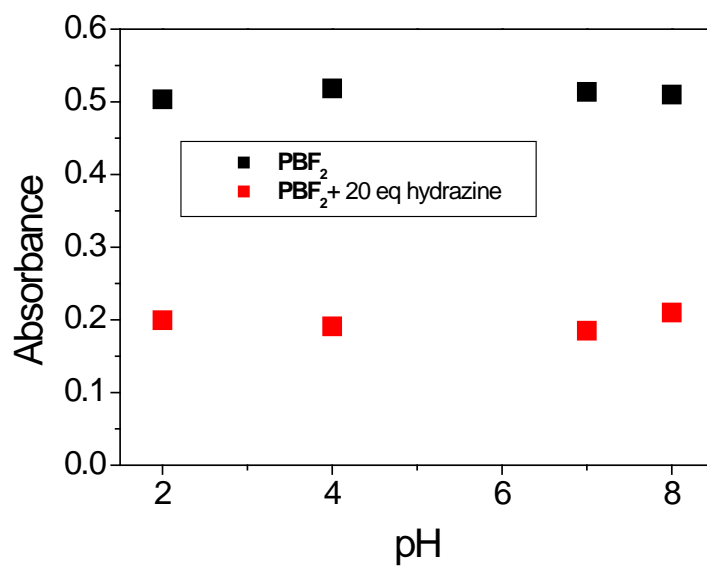


Figure S16. Changes of spectral intensity at different pH. The absorption intensity (490 nm) of PBF_2 (1×10^{-5} M) solutions in a mixture of acetate buffer (pH 4.0, 10 mM) and DMSO (1/9, v/v) with and without hydrazine (20 equiv.).