Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

A BODIPY Dye as Reactive Chromophric/Fluorogenic Probe for Selective and Quick Detection of Vapors of Secondary Amines

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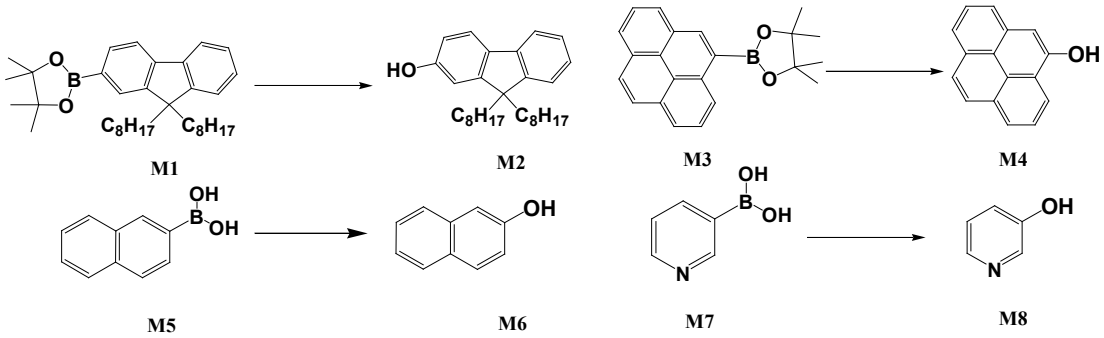
General: UV-vis absorption and fluorescence analysis were conducted on a Jasco V-670spectrophotometer and a Jasco FP 6500 spectrometer, respectively. The ^{1}H and ^{13}C NMR spectra were obtained from a Brucker DRX500 instrument, and tetramethylsilane (TMS) was used as an internal standard. Mass spectra were recorded on BIFLEX III MALDI-TOF (Brucker Daltonics Inc.) and GCT-MS Micromass UK mass spectrometers. All the films on (10×20 mm) quartz plates were spin-coated at 2500 rpm from their 1×10^{-2} M THF solutions, and placed in vacuum for 1 hour before use. The fluorescence responses of films to various analytes were progressed by inserting the films into sealed vials (3.8 ml) at room temperature containing cotton and analytes, which prevents direct film analyte contact and helps to maintain a constant

vapor pressure. The fluorescence time-course responses were recorded immediately after exposing the films to analytes by front-face (30°) detection. Quantum efficiencies of BODIPY 3 and BODIPY 4 in the solid state (films) were recorded on FLSP 920 fluorescence spectroscopy with a calibrated integrating sphere system.

Materials: All solvents and reagents were obtained from commercial sources and used as received.

Scheme S1



General synthesis of **M2**, **M4**, **M6**, **M8**

Excess secondary amine (4-20equiv.) was added to a solution of reactant **(M1**, **M3**, **M5 and M7)** in common solvents. The solution was stirred at room temperature for half an hour. Then the solvent was evaporated and the residue was purified by column chromatography on silica gel using CH_2Cl_2 as eluent to afford corresponding products with high yields (87%, 91%, 63% and 70% for **M2**, **M4**, **M6**, **M8**, respectively)

M2, ^{1}H-NMR(500MHz, $CDCl_3$, 25 ºC, TMS): δ=7.58-7.57(d, 1H, *J*= 7.25 Hz), 7.54-7.52(d, 1H, *J*= 8.05 Hz), 7.29-7.27(m, 2H), 7.24-7.19(m,

1H)，6.81 (d, 1H, *J* = 2.1Hz), 6.79-6.77(m，1H), 4.96(s, 1H), 1.96-1.84(m, 4H), 1.23-1.15(m, 4H), 1.12-1.03(m, 16H), 0.82-0.77(m, 6H), 0.64-0.57(m, 4H).

MS：MALDI-TOF 406.3

M4，^{1}H-NMR(500MHz, $CDCl_3$, 25ºC, TMS): δ=8.50-7.62(m, 9H), 5.64(s, 1H)

MS：EI 220

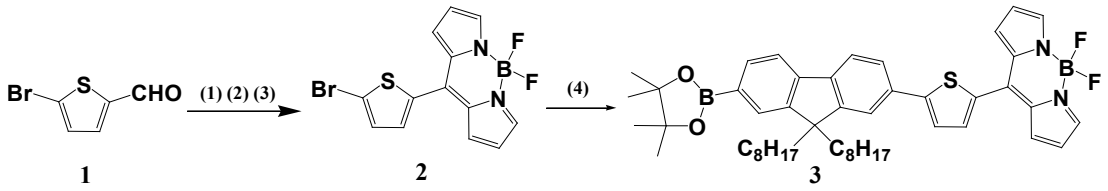
M6，^{1}H-NMR(500MHz，$CDCl_3$，25 ºC，TMS)：δ=8.36(s, 1H)，7.94(s 2H), 7.92-7.90(m, 2H), 7.58-7.55(m, 1H), 7.54-7.51(m, 1H), 6.12(s, 1H)

MS：EI 144

M8，^{1}H-NMR(500MHz，$CDCl_3$，25 ºC，TMS)：δ=8.31(s, 1H)，8.10(d, 1H, *J*= 4.35Hz), 7.33-7.27(m, 2H), 1.48-1.46(m, 1H)

MS：EI 95

Synthesis and Characterization



1 2 3

Synthesis of 8-(5-bromo-2-thienyl)-4, 4-difluoro-4-bora-3a, 4a-diaza -*s*-indacene 2:

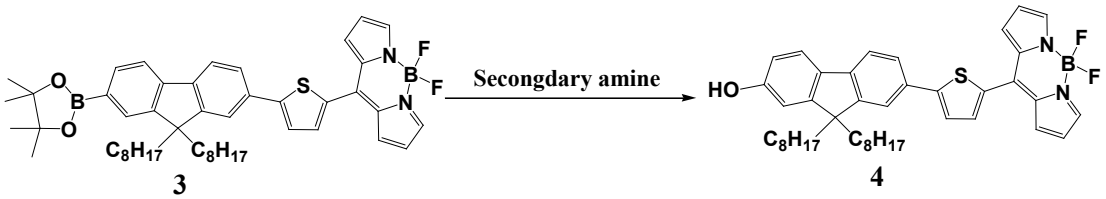
5-Bromo-2-thiophene carboxaldehyde (1.9 g, 10 mmol) and pyrrole(2.68 g，40 mmol) were dissolved in anhydrous methylene dichloride (30 mL) under argon atmosphere. One drop of trifluoroacetic acid was added, and the solution was stirred at room temperature

overnight. A solution of 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (4.54 g, 1mmol) in anhydrous methylene dichloride was added by a syringe, and the stirring was continued for another 4 hours. After the addition of triethylamine (15mL), $BF_3 \cdot OEt_2$ (15mL) was gradually added during 30 min in ace-water bath followed by continuous stirring at room temperature overnight. The reaction solution was shaken with 5% aqueous sodium bicarbonate (100ml), and the mixture was passed through a celite pad and washed with MC (30ml) to remove the black solid. The organic layer was washed with water and dried over anhydrous sodium sulfate. After concentration in vacuum, the residue was purified by flash chromatograophy twice, to afford a purple solid, Yield 28%. ^{1}H-NMR(500MHz, $CDCl_3$, 25 ºC, TMS): δ=7.926 (s, 2H)，7.31 (d, 1H, , J =2.15Hz), 7.25-7.22 (m, 3H), 6.57 (d, 2H, J =3.6Hz). ^{13}C NMR ($CDCl_3$) δ137.92, 135.83, 134.03, 133.10, 131.20, 119.17, 118.78, HRMS: calcd M^+ for $C_{13}H_8BN_2F_2SBr$ 351.9653; found 351.9657.

Synthesis of 7-(8-(4,4-difluoro-4-bora-3a,4a-diaza-s-indacene))- 2- (4, 4, 5, 5-tetramethyl-1, 3，2-dioxaborolan-2-yl) -9, 9 –dioctylfluorene **3**:

To a 1:1 mixture of 9, 9-dioctylfluorene-2, 7-bis (4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolane) and 8-(5-bromo-2-thienyl)-4, 4-difluoro-4-bora-3a, 4a-diaza-s-indacene, and tetra (triphenylphosphine)-palladium [$Pd(PPh_3)_4$](1.0 Mol %) in THF solution was added a degassed mixture of a drop of phase Aliquat 336 and 2 M

potassium carbonate aqueous solution. The mixture was stirred at 80℃ for 24 hours under the protection of argon. Then the solvent was evaporated and the residue was purified by column chromatography on silica gel using CH_2Cl_2 as eluent to afford burgundy solid (yield 33%). ^{1}H-NMR(500MHz, $CDCl_3$, 25ºC, TMS): δ=7.93(s, 2H), 7.84(d, 1H, *J* = 7.55 Hz), 7.77 (d, 2H, *J* = 7.9 Hz), 7.72(d, 1H, *J* =7.5 Hz), 7.68(d, 1H, *J* = 7.75 Hz), 7.61(d, 2H, *J* = 4.25 Hz), 7.54(d, 1H, *J*=3.65 Hz), 7.40(d, 2H, *J* = 3.7 Hz), 6.6 (d, 2H, *J* = 2.55 Hz), 2.0(m, 4H), 1.39(s, 12H), 1.20(m, 4H), 1.10-1.08 (m, 16H), 0.79(m, 6H), 0.62(m, 4H), ^{13}C NMR ($CDCl_3$) δ152.55, 152.29, 150.47, 150.19, 143.91, 143.35, 143.08, 142.29, 139.44, 134.72, 134.02, 133.94, 133.65, 133.43, 132.01, 131.06, 128.92, 125.18, 124.27, 120.84, 120.28, 119.31, 118.32, 83.807, 83.691, 55.405, 55.164, 40.186, 40.069, 31.754, 29.893, 29.686, 29.142, 24.934, 23.591, 22.563, HRMS: calcd M^+ for $C_{48}H_{60}B_2N_2O_2F_2S$ 788.4530; found 788.4540.



3 **4**

Synthesis of 7-(8-(4, 4-difluoro-4-bora-3a, 4a-diaza-s-indacene))-2-hydroxyl -9, 9 -dioctylfluorene **4**:

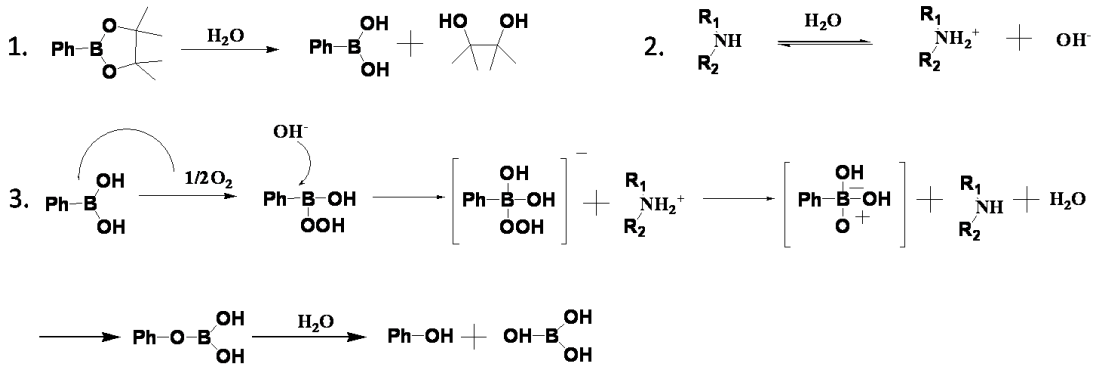
To a solution of **3** in CH_2Cl_2, excess secondary amine (4eq-20eq) was added, and then the solution was stirred at room temperature for half an

hour. After that, the solvent was evaporated and the residue was purified by column chromatography on silica gel using CH_2Cl_2 as eluent to afford purple solid with the yield of nearly 100%. ^{1}H-NMR(500MHz, $CDCl_3$, 25 ºC, TMS): δ=7.93 (s, 2H)，7.62-7.60 (m, 3H), 7.57-7.54 (m, 2H), 7.52 (d, 1H , J = 3.9 Hz), 7.42(d, 2H, J = 4.05 Hz), 6.84(d, 1H, J = 2.05 Hz), 6.79(m, 1H), 6.6(m, 2H), 2.02(m, 4H), 1.20(m, 4H), 1.10-1.06(m,16H),0.80 (m, 6H), 0.64(m, 4H), C^{13} NMR ($CDCl_3$) δ156.06, 153.47, 152.74, 151.31, 143.16, 142.49, 139.53, 134.87, 133.96, 133.22, 133.04, 131.03, 130.42, 125.22, 123.94, 121.02, 120.00, 119.43, 118.28, 114.29, 110.17, 55.24, 40.47, 31.75, 29.96, 29.68, 29.19, 24.89, 23.70, 22.56, 14.03, HRMS: calcd M^+ for $C_{42}H_{49}BN_2OF_2S$ 678.3627; found 678.3638.

Supporting results and discussion:

1 The reaction mechanism of secondary amine accelerating the oxidation of arylboronate(or aryl boronic acids) and the reason for why only the secondary amine can promote this reaction.

Scheme S2. Proposed reaction mechanism.



(1) Controlled experiments validate that the probe **3** cannot react with

secondary amine under the conditions without O_2 which indicate that O_2 acts as the oxidant during the reaction process.

(2) Many factors can affect the alkalinity of the organic amine. Among them, the inductive effect and the steric interaction play the key role to identify the alkalinity of organic amines. Customarily, the alkalinity of organic amine is secondary amine>primary amine> tertiary amine. For example, the pK_b's of methyl amine, dimethylamine, and trimethyl amine are 3.34, 3.27 and 4.19 respectively. Note that, in terms of pK_b, the strongest bases have the least positive values of pK_b. This also explains why the secondary amines can accelerate the oxidation of arylboronate(or aryl boronic acids) but primary and tertiary amines cannot.

(3) When the organic base is replaced by tetrabutyl ammonium hydroxide, a kind of organic strong base, this reaction occurs immediately. The color of the solution was observed to turn to violent first and then turn to yellow rapidly. This is because the new generated phenol is unstable in strong alkaline environment, and rapidly decomposes into sub-products. Finally, the TLC monitoring indicates the leftover in the solution is complex mixture. This explains that the final product phenol is obtained only when the organic amine with moderate strength like the secondary amine act as a catalyst.

Scheme S3. The yields of different reactions when BODIPY **3**(10 mM/L)

reacted with diversiform amines (40 equiv.) in THF solution for 10mins.

Entry	1	2	3	4	5	6	7
Yield	Trace	Trace	97%	100%	Trace	Trace	No

1 propylamine 2 hexylamine 3 diethylamine 4 diisopropylamine 5 triethylamine 6 benzylamine 7 aniline

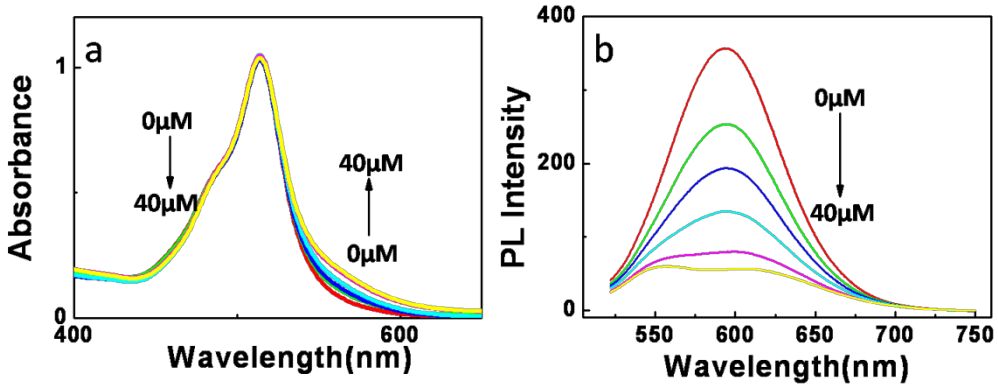


Fig. S1 Absorbance spectra (a) and Fluorescence spectra (b) of BODIPY **3** (20 μM) in the presence of increasing diethylamine concentrations (0, 8, 16, 24, 32, 40μM) in THF solution.

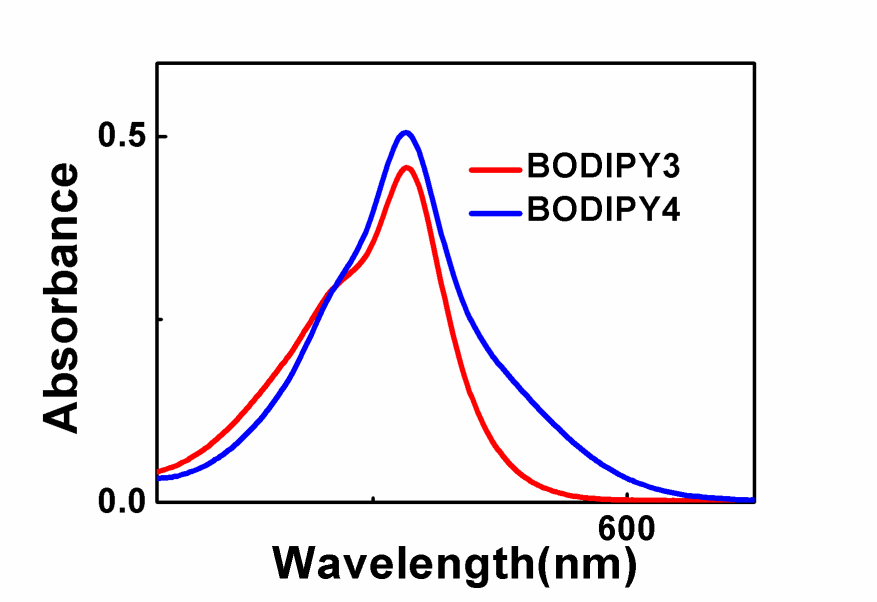


Fig S2 Absorption spectra of BODOPY **3** and BODOPY **4** (10μM) in THF solution.

2 The fluorescence quenching mechanism upon formation of phenol.

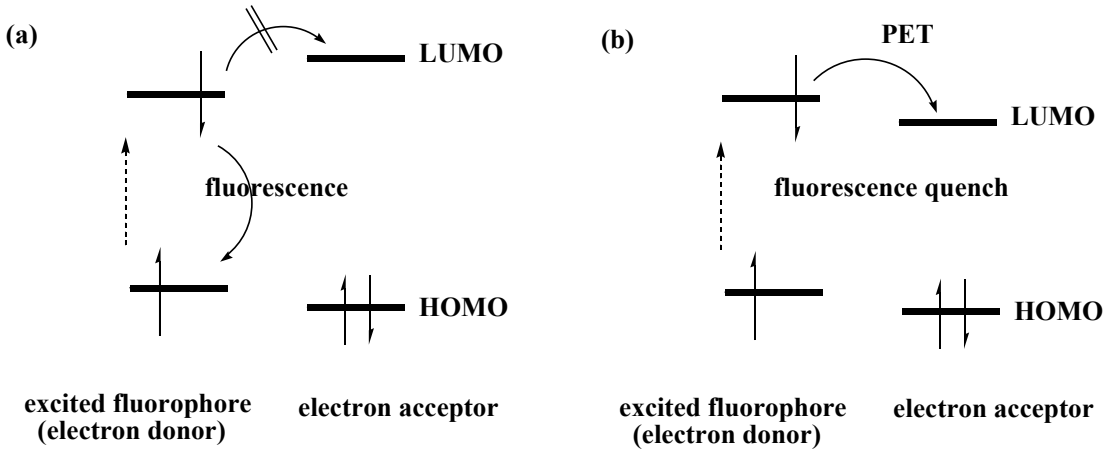


Fig S3. Schematic representation of PET strategy to control fluorescence. (a)the boronate ester acts as the electron acceptor; (b) the phenol acts as the electron acceptor.

The fluorescence quenching mechanism is a typical photo induced electron transfer (PET) mechanism [1]. In the BODIPY 3, the boronate ester acts as the electron acceptor and the BODIPY group acts as the fluorophore. The PET does not occur because the boronate ester has a higher LUMO energy level than the excited fluorophere. When the boronate ester is replaced by phenol, the new formed electron acceptor has a lower LUMO energy level than the excited fluorophere. Thus, the PET occurs and the fluorescence is quenched.

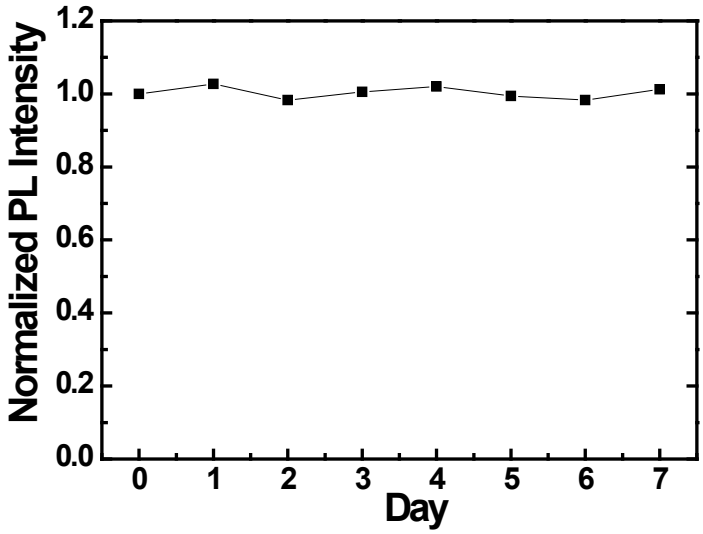


Fig S4 The fluorescence stability of the films made from BODIPY **3** after exposure in air.

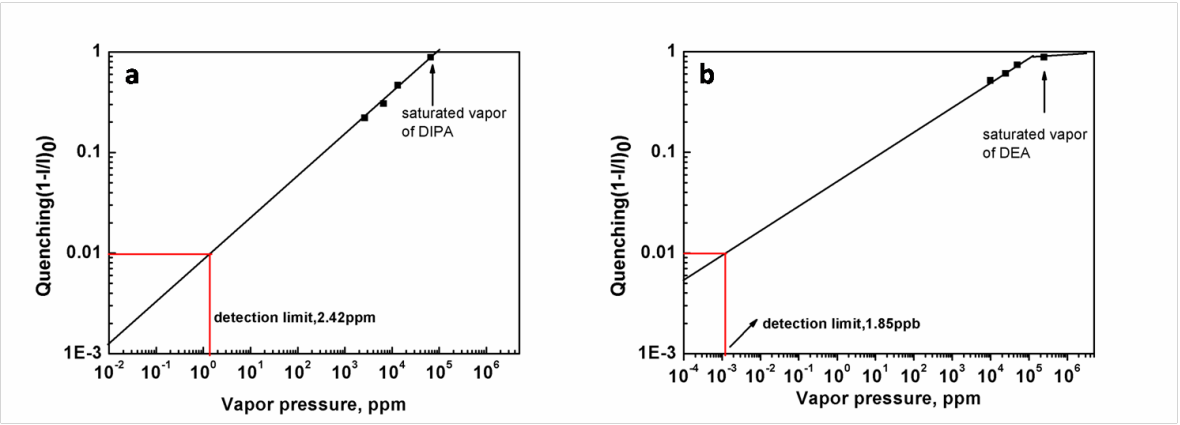


Fig S5 Fluorescence quenching efficiency ($1-I/I_0$) as a function of the vapor pressure of DIPA and DEA fitted with Langmuir equation.

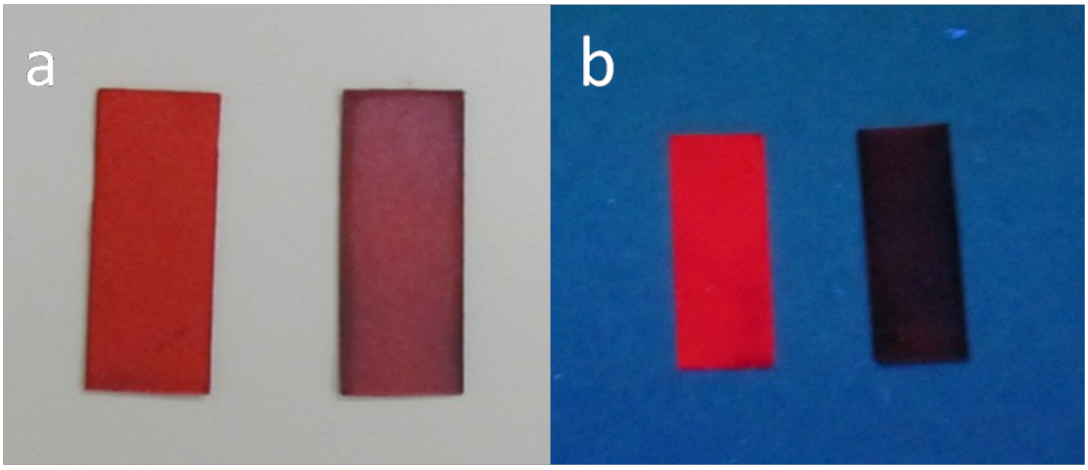


Fig S6 Color (a) and fluorescence (b) images of the test papers made from BODIPY **3** before and after exposure to saturated diisopropylamine vapor for 300s.

References

[1] M. Takuya, U. Yasuteru, T. Yoshinori, M. Yusuke, T. Takuya and N. Tetsuo, *J. Org. Chem.* 2011, **76**, 3616-3625