

Supporting Information

Organic microcrystal interface triggered reactivity: A case study of environmentally benign aromatic boric acid reaction

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Preparation methods

9-ANB microcrystal:

Based on the strategy rooted from the traditional solution phase recrystallization process, we used liquid–liquid interface precipitation method to gain 9-ANB microcrystal. 9-ANB was first dissolved in pure THF solvent to gain 1 mg/mL 9-ANB THF solution. Then distilled water was slowly added into the THF solution dropwise. The solution gradually became cloudy with blue fluorescence emission, together with the formation of microcrystals which can be observed by eyes. The optimum ratio of tetrahydrofuran to water for microcrystal formation was 1:3. In this condition, the microcrystal of 9-ANB can react with weak bases in highest rate. After a series of experiments, we found that only THF/H₂O mixed solvent could result in the microcrystal of 9-ANB with high reactivity while other organic solvents like ethanol, DMF and DMSO, showed no such effect, the morphology of amorphous 9-ANB film was shown in Figure S29.

9-ANB microcrystal SEM samples:

To show the main crystal plane exposed in the system, we directly collect the floating micro-nano crystals on the SiO₂ substrate, so that the measured XRD signals are relevant to the crystal faces in the reaction system. First, we dropped a droplet of 9-ANB micronano-crystal system onto the SiO₂ substrate and immediately remove it in less than 1 second, then all liquid phase could be removed due to the hydrophobic surface, and the situ micro-nano structure can be directly observed by SEM.

9,10-anthraquinone:

22.2 mg (0.1 mmol) 9-ANB was added in 100 mL tetrahydrofuran, then 300 mL distilled water was added. Then 4.8 mg (0.12 mmol) NaOH was added in the solvent. Here NaOH can be replaced by other strong or weak bases, such as *n*-propylamine, diethylamine, or triethylamine, etc. The color of the solvent changes from colorless to yellow immediately, and the fluorescent color changed from blue to yellow. After stirred at room temperature for about 1 hour, the solution turned to be transparent and the fluorescence disappeared. Most of the product 9,10-anthraquinone was gained by filtration as pure precipitation from the solvent. After evaporation and extraction purification steps, 20.6 mg (yield, 99.03%) 9,10-anthraquinone was gained as light-yellow powder with no fluorescence.

All solvents and reagents were purchased from commercial sources and used as received. NMR spectra were measured with Bruker DRX500 instrument, using tetramethylsilane (TMS) as the internal standard substance. Crystal structure was measured with Bruker APEX-II CCD diffractometer. UV–Vis absorption spectra were measured with Jasco V-670 spectrophotometer, while phosphorescence and fluorescence spectra were measured with HORIBA Fluoro-Max 4 spectrometer. Scanning Electron Microscope (SEM) images were taken with JEOL 7800F. The isotope-labeling reactants of ¹⁸O₂ (97% atom% ¹⁸O) was purchased from Shanghai Research Institute of Chemistry Industry Co, Ltd. The isotope-labeling concentration of products was established by isotopic mass spectrometry from Shanghai Research Institute of Chemistry Industry Co, Ltd.

Fluorescence photos of 9-ANB isotope labelling experiment

We added isotopic experiments with ¹⁸O₂ in the reaction system. Here we used ¹⁸O₂ instead of the suggested oxygen-17 enriched water. The oxygen resource and isotopic measurement are both from Shanghai Research Institute of Chemistry Industry Co, Ltd.



Figure S1. Fluorescent photos of the 9-ANB crystal system after base addition: (a) reaction system without adding oxygen; (b) 50 minutes after adding oxygen ($^{18}\text{O}_2$) (c) comparison group without adding oxygen overnight.

After careful anoxic treatment, the reaction system was prepared in a Double buccal bottle under the protection of Argon. After addition of amine, the microcrystal system rapidly changed into yellow solution with bright yellow fluorescence. Such fluorescent intermediate state remained stable overnight without the existence of oxygen. Therefore, oxygen was a necessary reactant for the second step reaction.

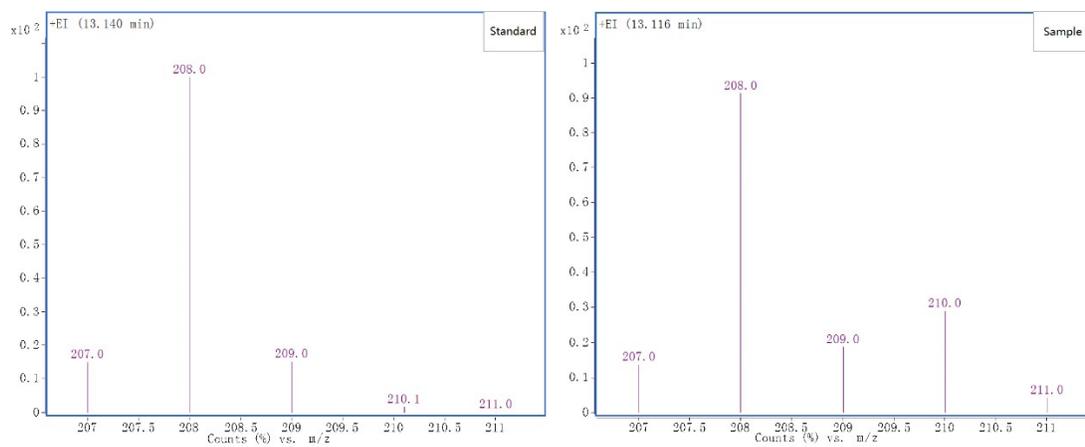


Figure S2. The EI mass spectra of the standard anthraquinone and the isotope labelled sample.

Compared with the natural oxygen, the ^{18}O atom% was increased from 0.11% to 24.14%. Hence the $^{16}\text{OH}^-$ ion in solution may probably act an important role in the rearrangement and departure reaction process. In the rearrangement and departure process, the ^{18}O and ^{16}O have equal possibility to keep attaching with the carbon atom, leading to nearly 25% atom percent of ^{18}O . The probable reaction process between active intermediate and dissolved oxygen in solution is as followed in Figure S3.

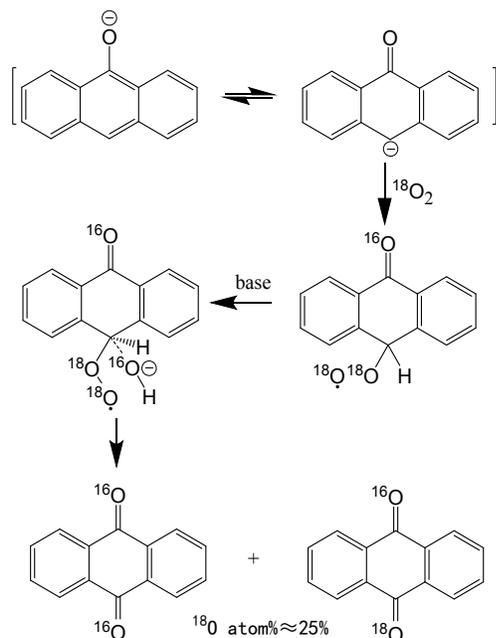


Figure S3. The probable reaction process between active intermediate and dissolved oxygen in solution.

Simulation configurations

Forcite Dynamics

Table S1 Forcite Dynamics parameters

Ensemble	: NVE
Temperature	: 298.00 K
Timestep	: 1.00 fs
Number of steps	: 50000
Duration	: 50 ps
Initial velocities	: Random
Random number seed	: 1576485843
---- Energy parameters ----	
Forcefield	: Dreiding
Charges	: Use current
Electrostatic terms:	
Summation method	: Atom based

Truncation method : Cubic spline
Cutoff distance : 18.5 Å
Spline width : 1 Å
Buffer width : 0.5 Å

van der Waals terms:

Summation method : Atom based
Truncation method : Cubic spline
Cutoff distance : 18.5 Å
Spline width : 1 Å
Buffer width : 0.5 Å

Hydrogen bond terms:

Summation method : Atom based
Truncation method : Cubic spline
Cutoff distance : 4.5 Å
Spline width : 0.5 Å
Buffer width : 0.5 Å

---- Constraints ----

Position constraints : 224

---- Dynamics summary ----

	Initial	Final	Average	Std. Dev.
Tot. energy (kcal/mol)	38.319	38.774	38.628	0.083
Pot. energy (kcal/mol)	18.776	23.390	24.199	2.346
Kin. energy (kcal/mol)	19.542	15.384	14.429	2.299
Tot. enthalpy (kcal/mol)	38.319	38.774	38.628	0.083
Temperature (K)	298.000	234.594	220.023	35.050
Area (Å ²)	165.473	165.473	165.473	0.000
Surface density (amu/Å ²)	11.347	11.347	11.347	0.000

Task terminated : Mon Dec 16 16:44:15 2019

Total CPU time used by Forcite: 12 seconds (12.37s)

Termination status : Normal

Job Name : 3D_Atomic

Task : Property
 Basis : dnp
 Atom_Rcut : 4.100 Angstrom
 Functional : blyp
 Harris : off
 Integration Grid : fine
 Occupation : fermi
 Pseudopotential : none
 Property : Optics (TDDFT)
 Iteration : 14
 Convergence : 0.0000083 Ha

hkl	Multiplicity	dhkl	Surface area	Surface	Eatt(Total)	Eatt(vdW)	Eatt(Electrostatic)	Eatt(H-bond)	Distance	Total facet area	% Total facet area
{ 0 0 2}	2	16.11965000	82.73662884	 Surface (0 0 2)	-30.36607478	0.33501339	0.00000000	-30.70108817	30.36607478	7.793394e+004	52.86636184
{ 0 1 1}	4	14.74991589	180.83974293	 Surface (0 1 1)	-54.70650911	-47.03123707	0.00000000	-7.67527204	54.70650911	5.598774e+004	37.97919657

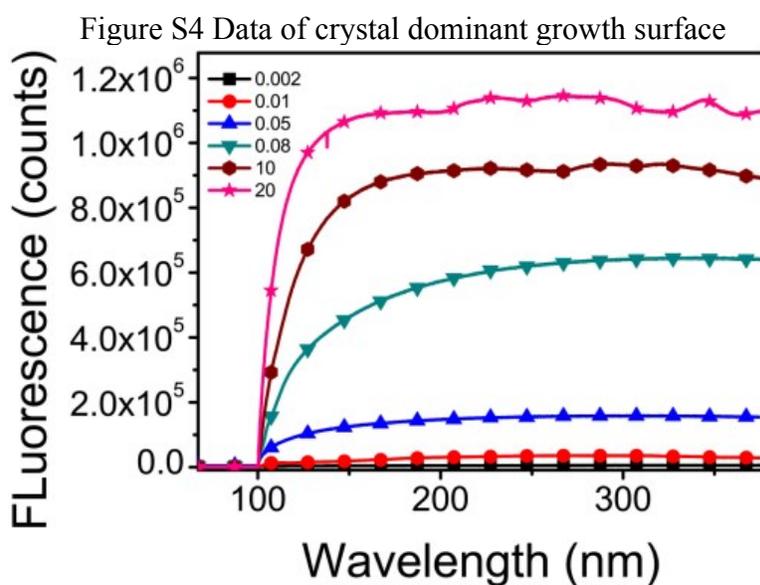


Figure S5. The fluorescence enhancement curves of 9-ANB microcrystal system with different amine addition amount

The Single-crystal data of 9-ANB and 9,10-anthraquinone

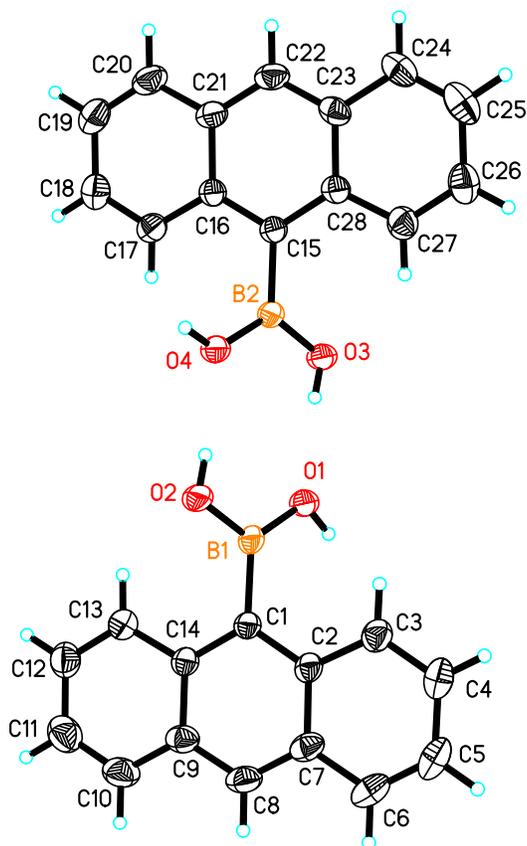


Figure S6 The Single-crystal data of 9-ANB

Table S2. Crystal data and structure refinement for 9-ANB.

Identification code	mo_d8v19766_0m	
Empirical formula	$C_{28}H_{22}B_2O_4$	
Formula weight	444.07	
Temperature	293(2) K	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	$a = 4.9878(3) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 16.5878(10) \text{ \AA}$	$\beta = 90^\circ$
	$c = 32.2393(18) \text{ \AA}$	$\gamma = 90^\circ$

Volume	2667.4(3) Å ³
Z	4
Density (calculated)	1.106 mg/m ³
Absorption coefficient	0.072 mm ⁻¹
F(000)	928
Crystal size	0.170 * 0.140 * 0.100 mm ³
Theta range for data collection	2.258° to 25.494°
Index ranges	-5<=h<=6, -20<=k<=15, -39<=l<=38
Reflections collected	12556
Independent reflections	4885 [R(int) = 0.0416]
Completeness to theta = 25.242°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5952
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4885 / 4 / 324
Goodness-of-fit on F ²	1.047
Final R indices [I>2sigma(I)]	R ₁ =0.0678, wR ₂ =0.1818
R indices (all data)	R ₁ =0.0917, wR ₂ =0.1971
Absolute structure parameter	0.1(10)
Extinction coefficient	0.025(5)

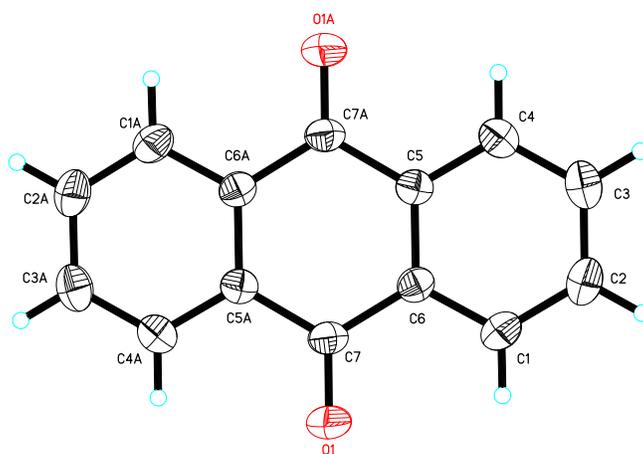


Figure S7 The Single-crystal data of 9,10-anthraquinone

Table S3. Crystal data and structure refinement for 9,10-anthraquinone.

Identification code	mo_d8v19420_0m	
Empirical formula	C ₁₄ H ₈ O ₂	
Formula weight	208.20	
Temperature	293(2) K	
Crystal system	Monoclinic	
Space group	P2 ₁ /C	
Unit cell dimensions	a = 7.8678(3) Å	α = 90°
	b = 3.9743(2) Å	β = 102.666(2)°
	c = 15.8041(6) Å	γ = 90°
Volume	482.15(4) Å ³	
Z	2	
Density (calculated)	1.434 mg/m ³	
Absorption coefficient	0.096 mm ⁻¹	
F(000)	216	
Crystal size	0.200 x 0.120 x 0.080 mm ³	
Theta range for data collection	4.137° to 25.997°	

Index ranges	-9<=h<=9, -4<=k<=4, -19<=l<=17
Reflections collected	4365
Independent reflections	929 [R(int) = 0.0382]
Completeness to theta = 25.242°	98.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6413
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	929 / 0 / 74
Goodness-of-fit on F ²	1.060
Final R indices [I>2sigma(I)]	R ₁ = 0.0388, wR ₂ = 0.1059
R indices (all data)	R ₁ = 0.0472, wR ₂ = 0.1142

Reaction data of aromatic boric acids with triethylamine addition (μL)

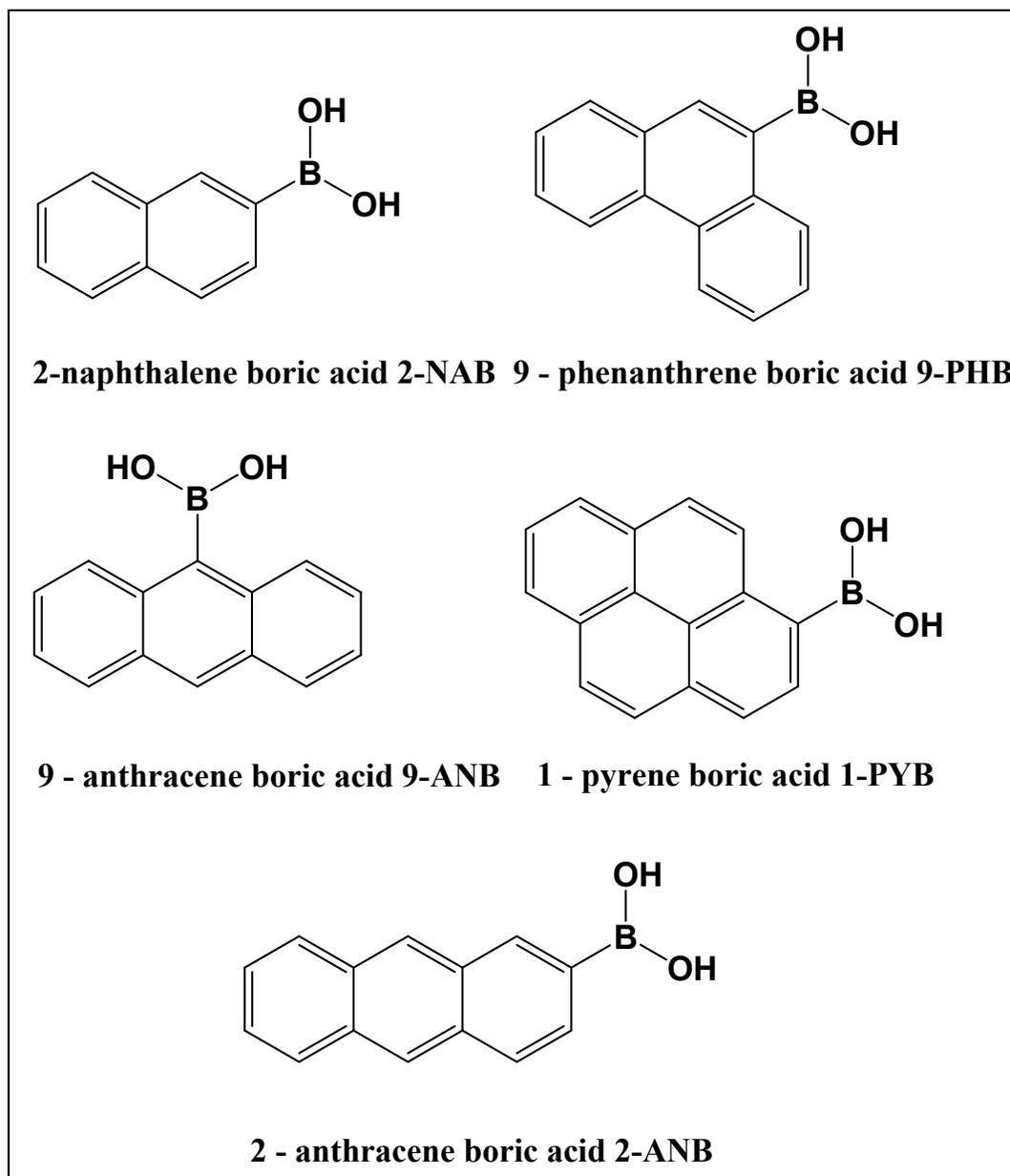


Figure S8 Molecule structures of aromatic boric acids

Molecule structures of 2-naphthalene boric acid (2-NAB) , 9 - anthracene boric acid (9-ANB) , 9 – phenanthrene boric acid (9-PHB) and 1 - pyrene boric acid (1-PYB) are shown in Figure S8.

2-NAB

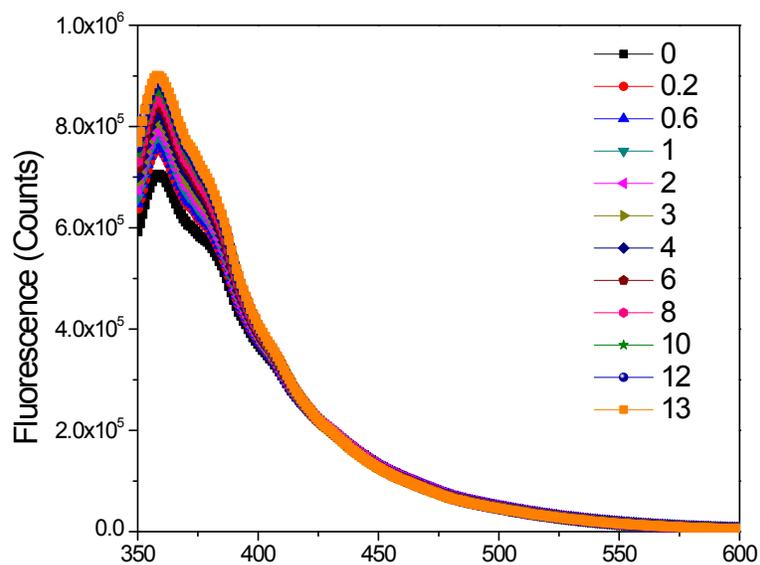


Figure S9 Fluorescence spectra of 1 mg/mL 2-NAB THF solution, THF/H₂O (1:0, v/v).

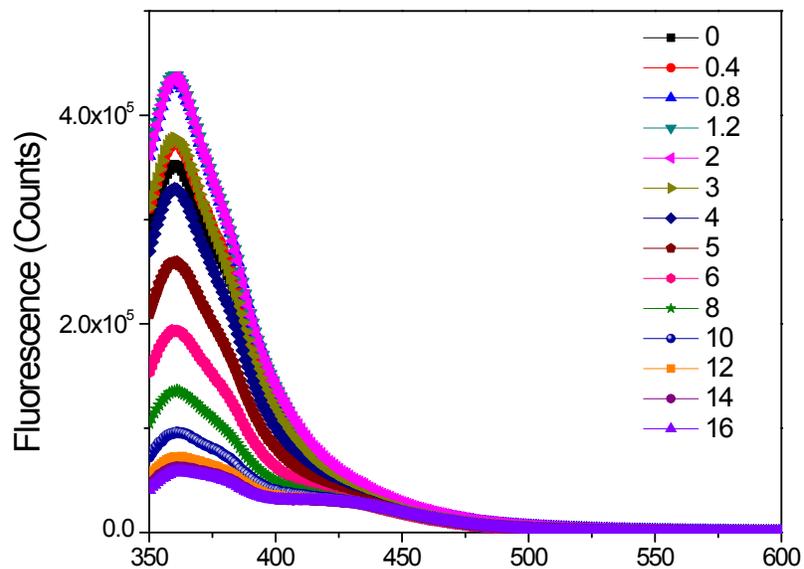


Figure S10 Fluorescence spectra of 2-NAB in 1 mg/mL THF/H₂O (1:1, v/v) mixture.

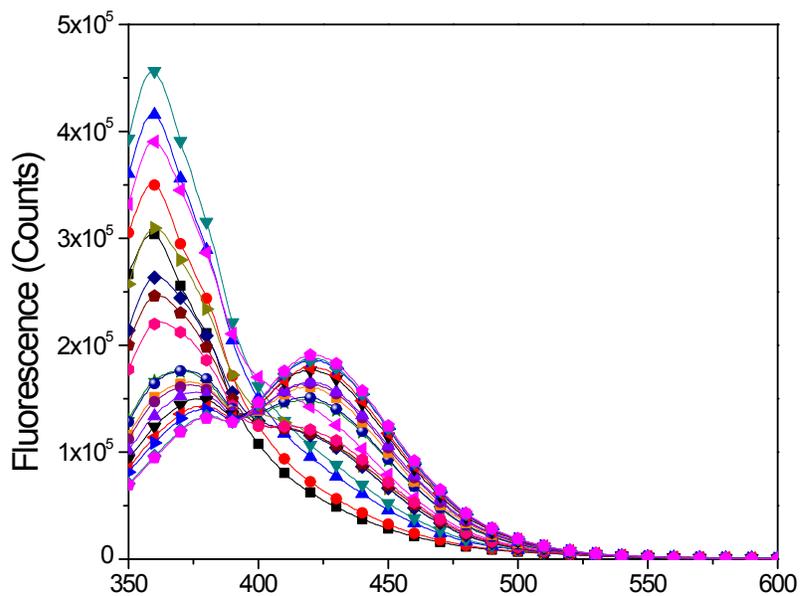


Figure S11 Fluorescence spectra of **2-NAB** in 1 mg/mL THF/H₂O (1:2, v/v) mixture.

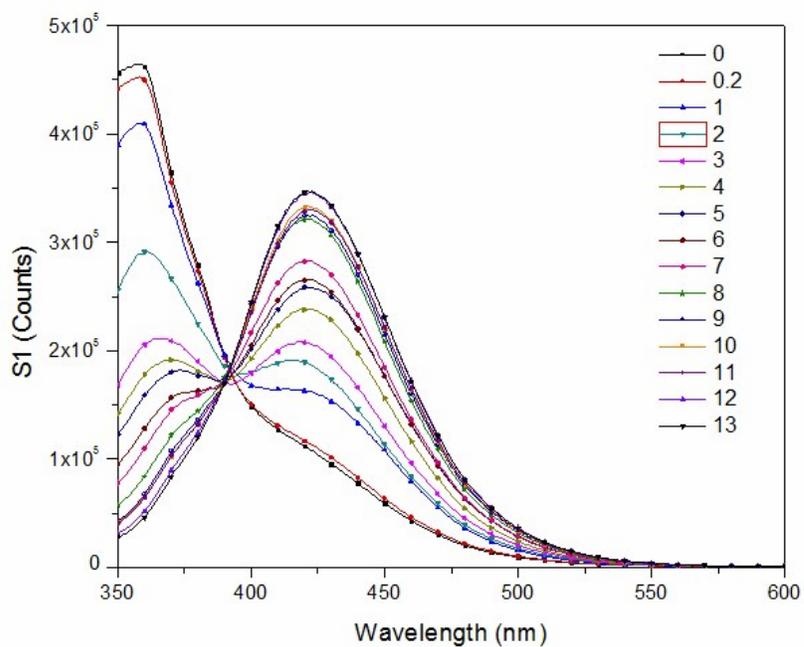


Figure S12 Fluorescence spectra of **2-NAB** in 1 mg/mL THF/H₂O (1:3, v/v) mixture.

9-ANB

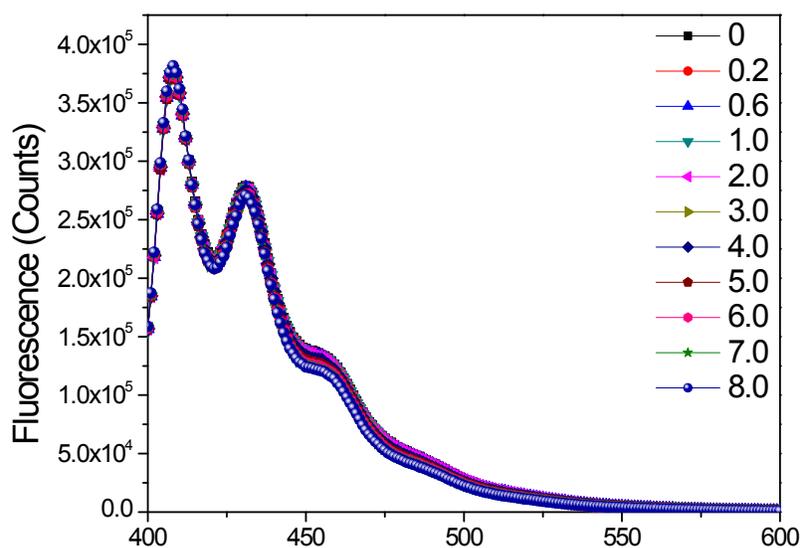


Figure S13 Fluorescence spectra of 1 mg/mL 9-ANB THF solution, THF/H₂O (1:0, v/v).

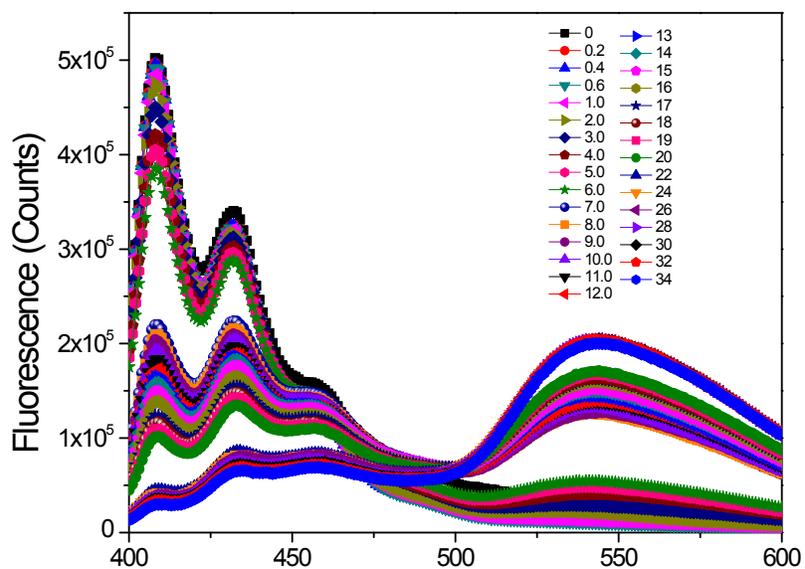


Figure S14 Fluorescence spectra of 9-ANB in 1 mg/mL THF/H₂O (1:1, v/v) mixture.

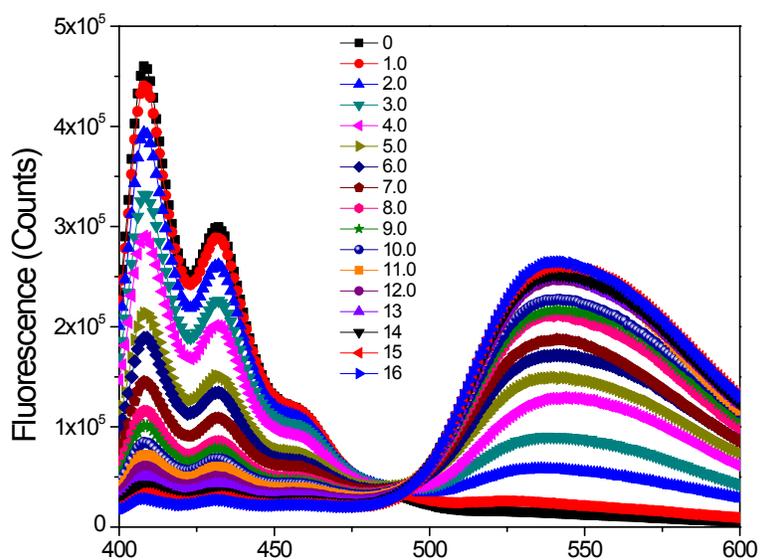


Figure S15 Fluorescence spectra of **9-ANB** in 1 mg/mL THF/H₂O (1:3, v/v) mixture.

9-PHB

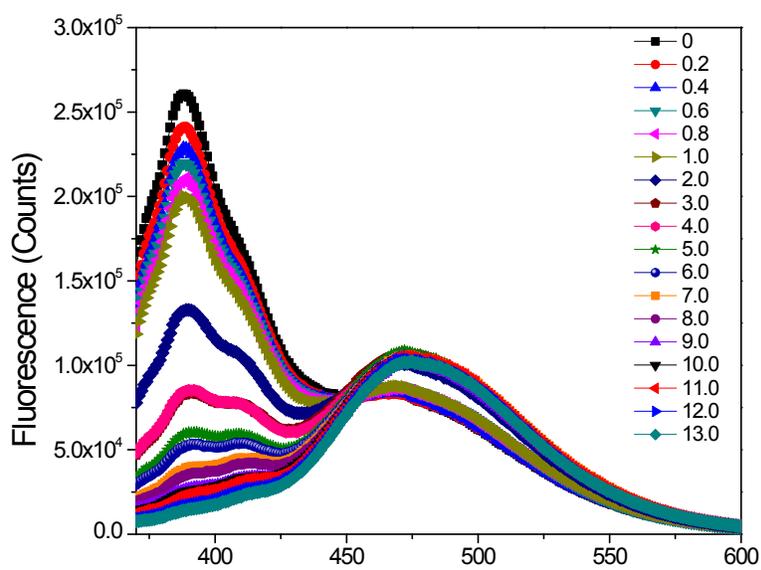


Figure S16 Fluorescence spectra of **9-PHB** in 1 mg/mL THF/H₂O (1:3, v/v) mixture.

1-PYB

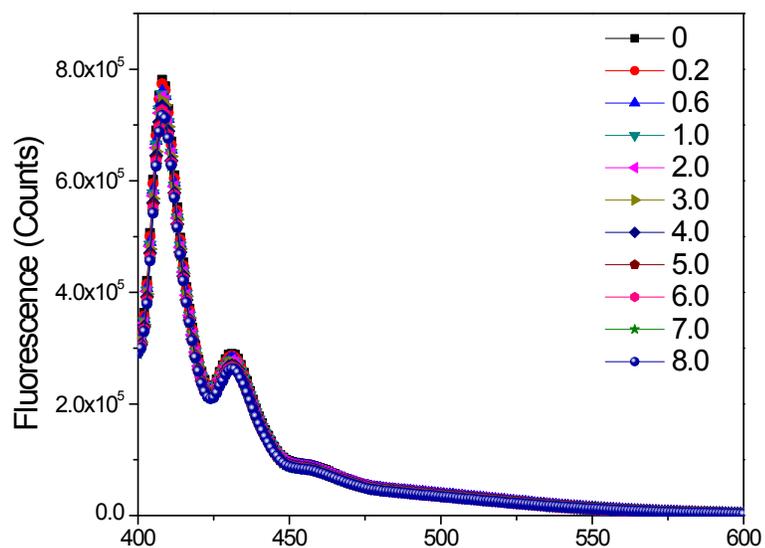


Figure S17 Fluorescence spectra of 1 mg/mL **9-PYB** THF solution, THF/H₂O (1:0, v/v).

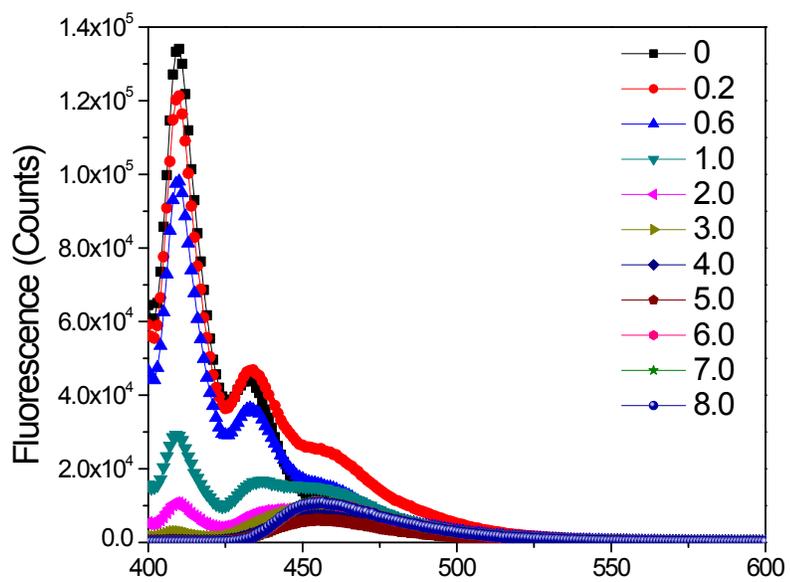


Figure S18 Fluorescence spectra of **9-PYB** in 1 mg/mL THF/H₂O (1:1, v/v) mixture.

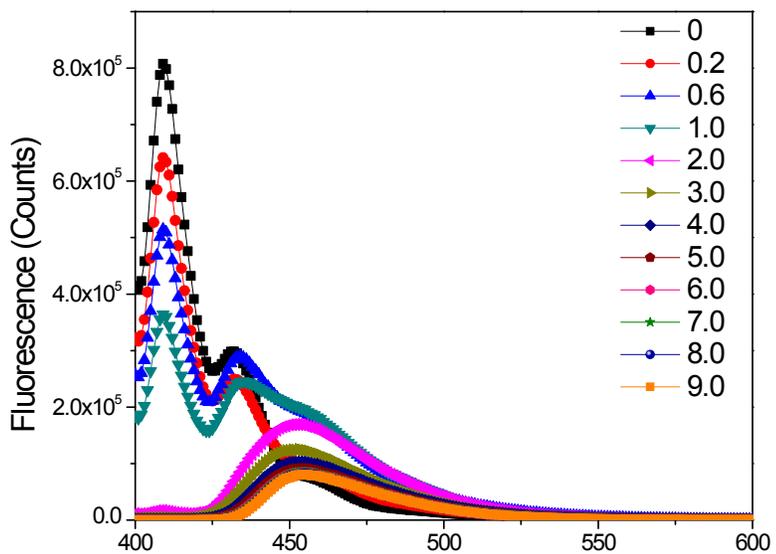


Figure S19 Fluorescence spectra of **9-PYB** in 1 mg/mL THF/H₂O (1:2, v/v) mixture.

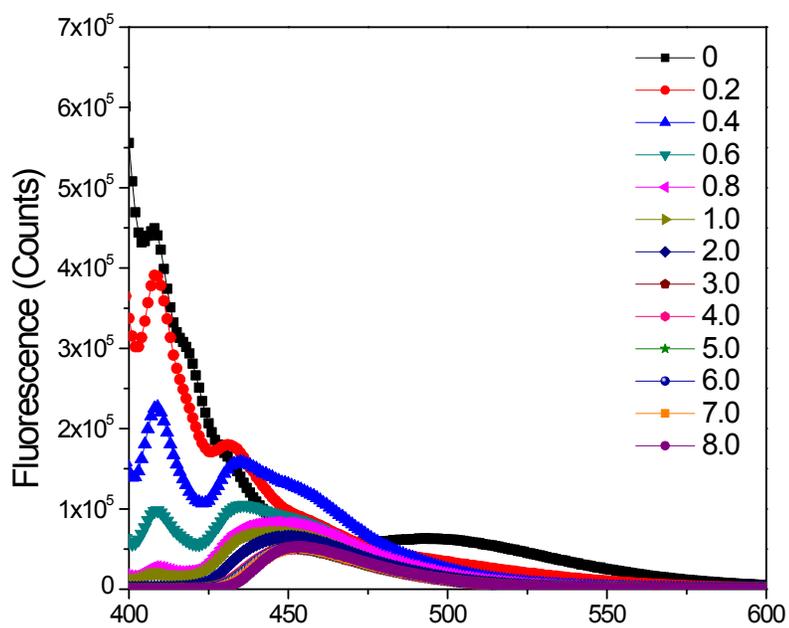


Figure S20 Fluorescence spectra of **9-PYB** in 1 mg/mL THF/H₂O (1:3, v/v) mixture.

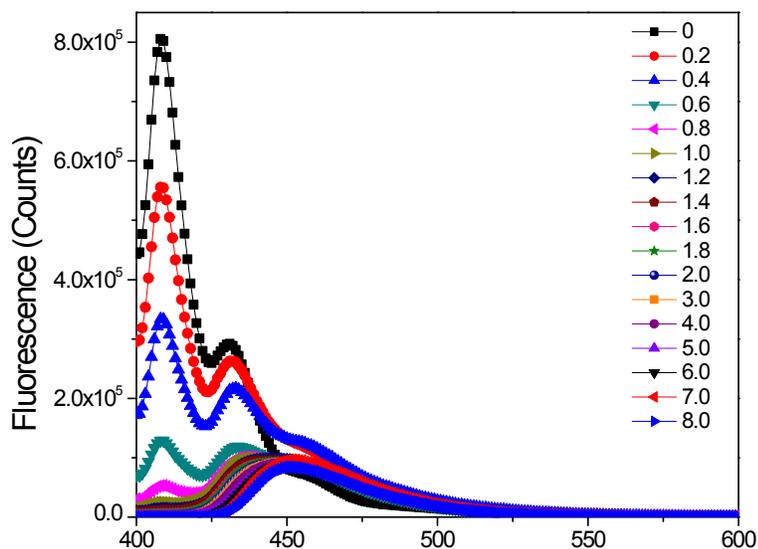


Figure S21 Fluorescence spectra of **9-PYB** in 1 mg/mL THF/H₂O (1:4, v/v) mixture.

Additional time related reaction monitoring data

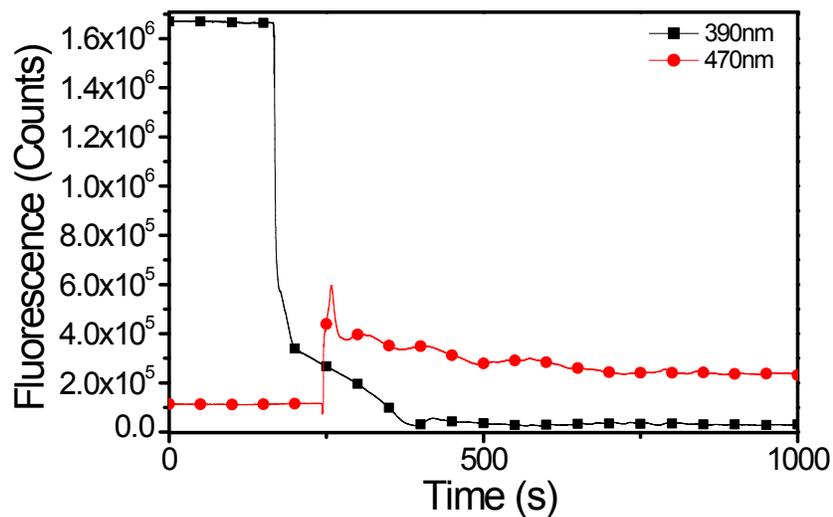


Figure S22 Fluorescence time curves of **9-PHB** in 1 mg/mL THF/H₂O (1:3, v/v) mixture after adding 2 μ L Et₃N at 390nm and 470 nm, excited at 350nm.

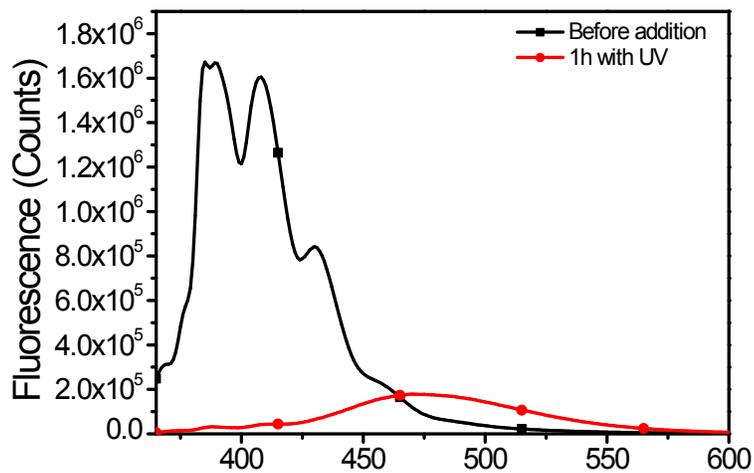


Figure S23 Fluorescence spectra of **9-PHB** in 1 mg/mL THF/H₂O (1:3, v/v) mixture before adding 2 μL Et₃N and after complete reaction.

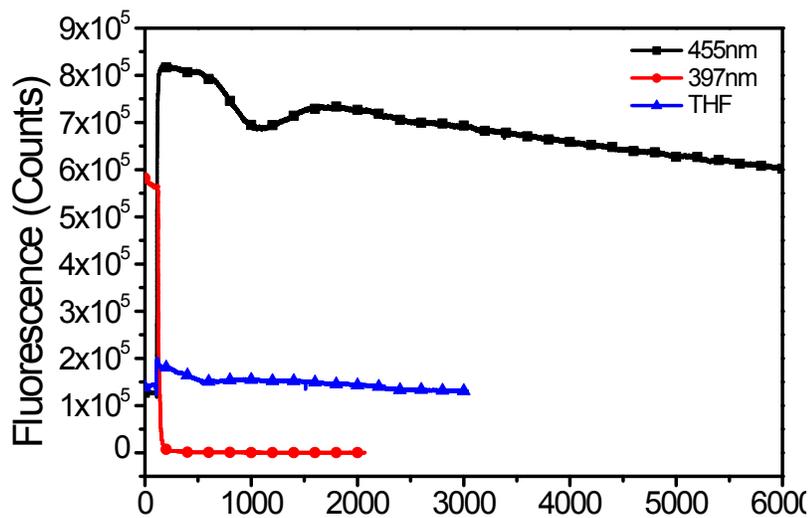


Figure S24 Fluorescence time curves of **9-PYB** in 1 mg/mL THF/H₂O (1:3, v/v) mixture after adding 2 μL Et₃N at 390nm and 455 nm, and time curve in pure THF at 390nm excited at 350nm.

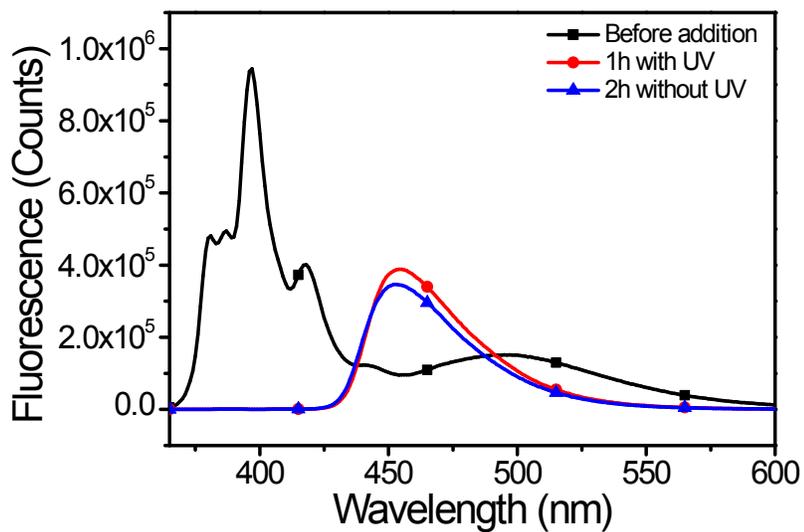


Figure S25 Fluorescence spectra of 9-PYB in 1 mg/mL THF/H₂O (1:3, v/v) mixture before adding 2 μL Et₃N and after complete reaction.

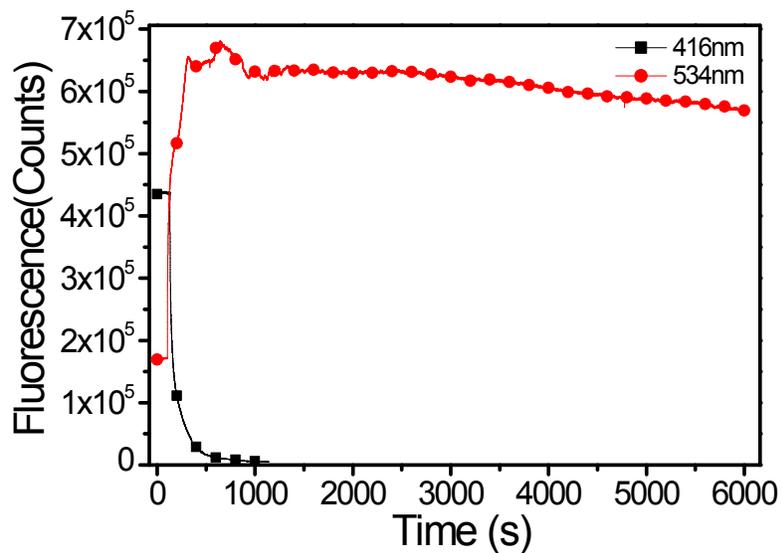


Figure S26 Fluorescence time curves of 2-ANB in 1 mg/mL THF/H₂O (1:3, v/v) mixture after adding 2 μL Et₃N at 416 nm and 534 nm, excited at 350 nm.

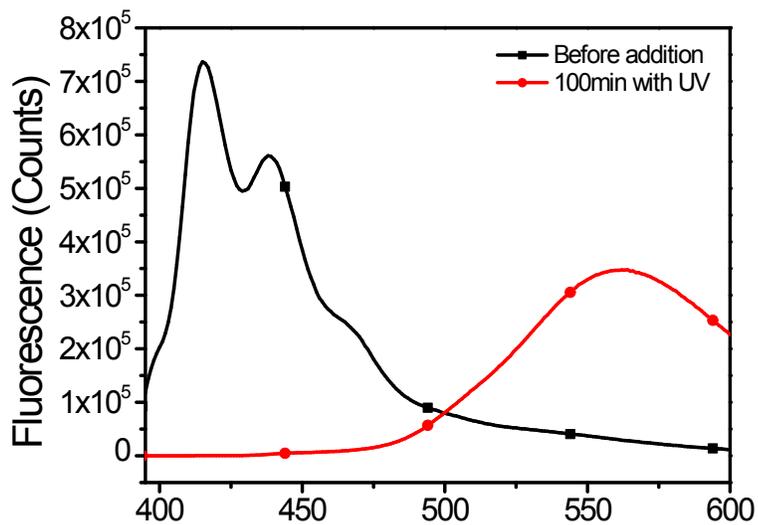


Figure S27 Fluorescence spectra of 2-ANB in 1 mg/mL THF/H₂O (1:3, v/v) mixture before adding 2 μ L Et₃N and after complete reaction.

SEM photos of the micro-nano system.

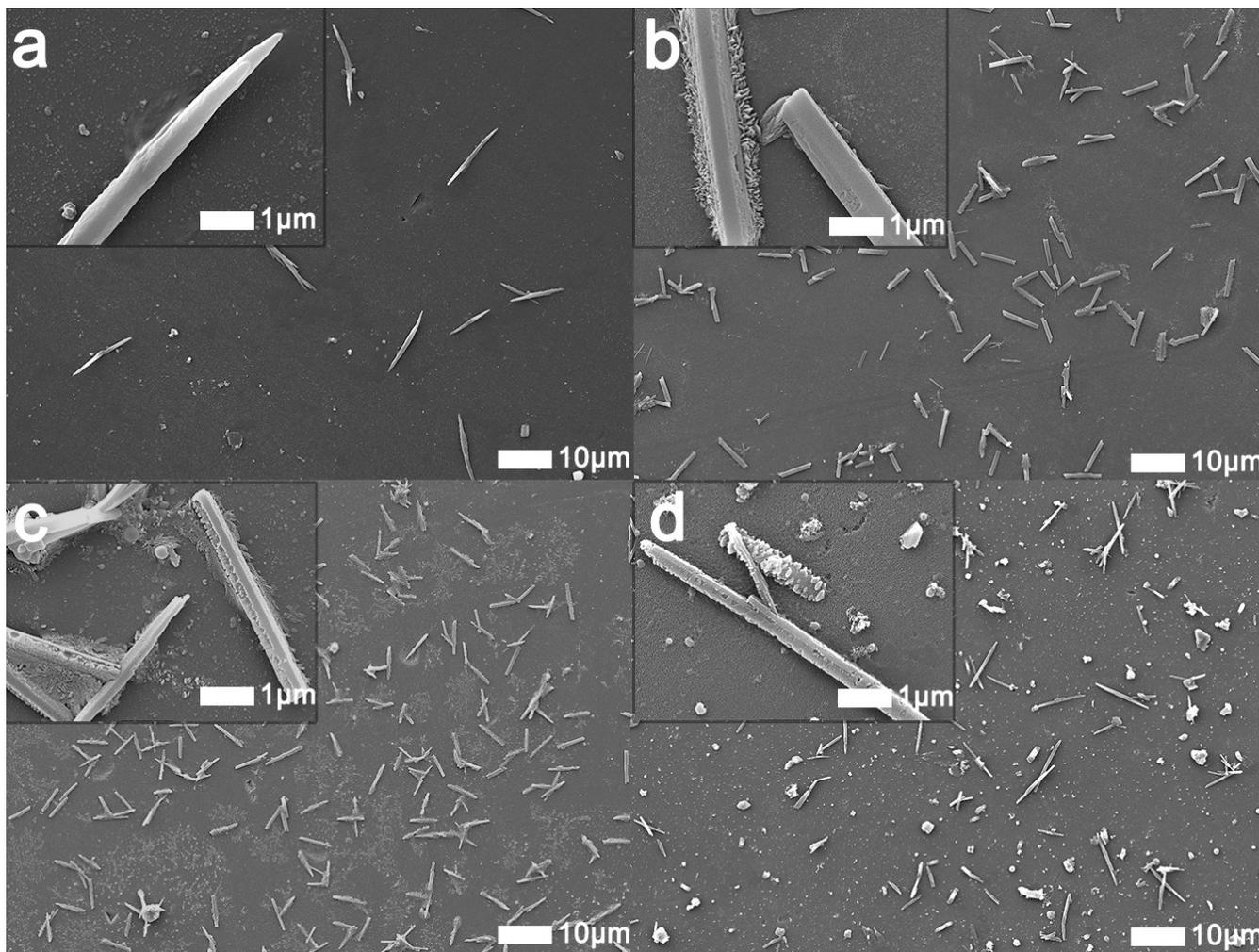


Figure S28 SEM photos of self-assembled 9-ANB in 1 mg/mL THF/H₂O (1:3, v/v) mixture (a) before and after addition of (b) 4.5 μ L, (c) 9 μ L and (d) 13.5 μ L 40 mg/mL NaOH.

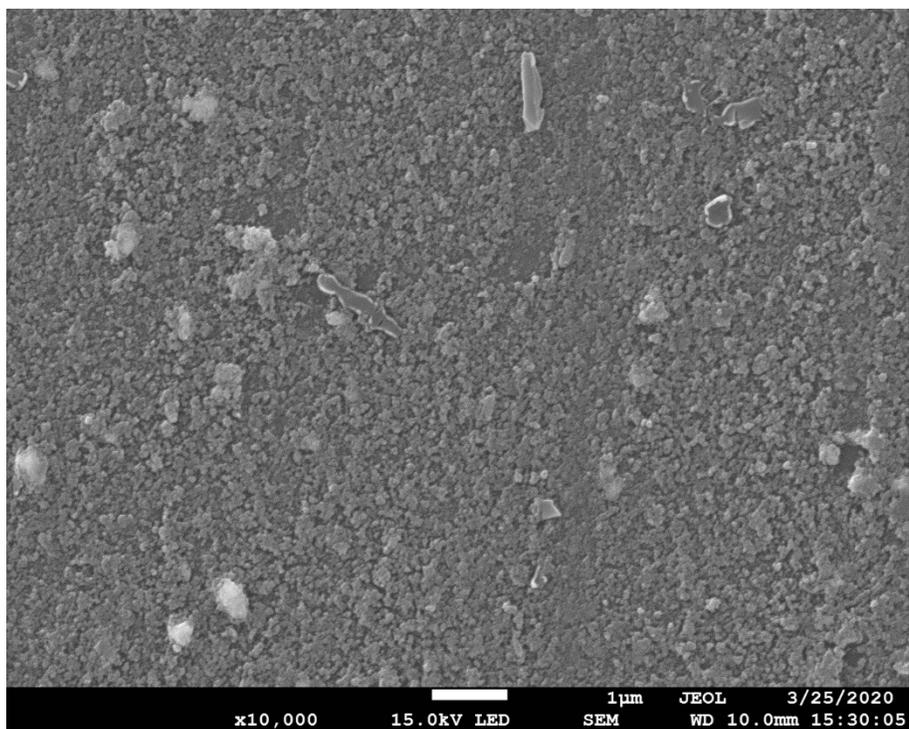


Figure S29 SEM image of complete amorphous 9-ANB, gained in 1 mg/mL EtOH/H₂O (1:3, v/v) mixture.