Electronic Supplementary Information (ESI)

for

Solvatofluorochromic flavonoid dyes with enlarged transition dipole moments enable ratiometric detection of methanol in commercial biodiesel with improved sensitivities

Tianyi Qin,[ab] Bin Liu,[b]* Bing Du,[b] Yingying Huang,[b] Guangkai Yao,[a] Zhiqing Xun,[c] Hanhong Xu[a]* and Chen Zhao[a]*

[a] State Key Laboratory for Conservation and Utilization of Subtropical Agro-bioresources, Key Laboratory of Natural Pesticide and Chemical Biology of the Ministry of Education, South China Agricultural University, Guangzhou, 510642, Guangdong, China.

[b] Shenzhen Key Laboratory of Polymer Science and Technology, Guangdong Research Center for Interfacial Engineering of Functional Materials, College of Material Science and Engineering, Shenzhen University, Shenzhen, 518060, China.

[c] Guangzhou Quality Supervision and Testing Institute, 1-2 Zhujiang Rd, Guangzhou, 511447, China.

Corresponding Authors: Prof. Bin Liu, bliu@szu.edu.cn; Prof. Hanhong Xu, hhxu@scau.edu.cn; Prof. Chen Zhao, zhaoc@scau.edu.cn

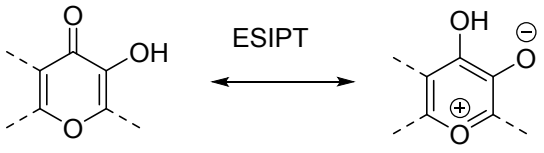
Synthesis

N,N-diethyl-3-hydroxy-2-naphthamide (**1**). $SOCl_2$ (100 ml, 1 mol/L, 2.0 e.q.) and 3-hydroxy-2-naphthoic acid (10 g, 0.053 mol, 1 e.q.) were mixed at the N_2 atmosphere and stirred under reflux for 4 h. After cooling to the room temperature and removing the excess $SOCl_2$ in vacuum, the oily residue was obtained as crude acid chloride. A solution of the oily residue in 10 ml CH_2Cl_2 was added dropwisely into a mixture of diethylamine (15.9 g, 0.26 mol, 5 e.q.) and 4-dimethylaminopyridine (0.1 e.q.) in 40 ml CH_2Cl_2 at 0 ℃ under the Ar atmosphere. After stirring at room temperature for 10 h, the mixture was poured into 400 ml HCl (1 mol/L) solution and extracted with CH_2Cl_2 (3 × 50 ml). Evaporating the solvents afforded the crude products, which were purified by recrystallizing from n-hexane/acetone mixture as white solid (10 g, 73%). ^{1}H-NMR (600 MHz, DMSO-*d*6) δ: 10.05 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.66 (s, 1H), 7.41 (t, *J* = 8.1 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.18 (s, 1H), 3.47 (m, 2H), 3.12 (m, 2H), 1.17 (m, 3H), 0.99 (m, 3H). ^{13}C-NMR (150 MHz, DMSO-*d*6), δ: 168.12, 151.94, 134.65, 128.70, 128.14, 127.73, 126.97, 126.94, 126.21, 123.64, 109.49, 56.64, 18.93. MS (HR ESI-TOF): m/z: calcd for $C_{15}H_{18}NO_2^+$ $[M+H]^+$: 244.1332; found: 244.1329.

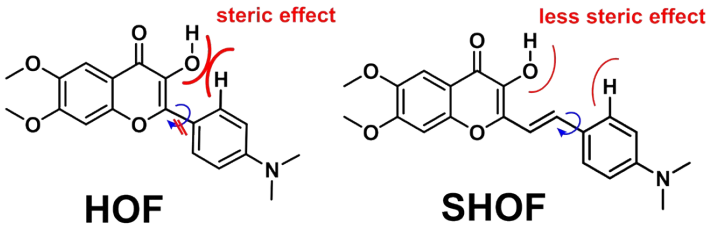
1-(3-hydroxynaphthalen-2-yl)ethan-1-one (**2**). Trimethylsilyl chloride (4.5 g, 0.042 mol, 1.2 e.q.) was added dropwisely to a vigorously stirred solution of **1** (9 g, 0.035 mol, 1 e.q.) and lithium diisopropylamide (70 ml, 0.14 mol, 4 e.q.) in extra dry THF under the Ar atmosphere with an ice-water bath. The reaction was stirred at 0 ℃ for

30 minutes and then the ice-water bath was removed. After stirring for another 30 minutes when the temperature gradually rose to the room temperature. The Schlenk flask was cooled down to 0 ℃ again with the addition of 100 ml HCl (1 mol/L) for quenching. The mixture was extracted with ethyl acetate (3 × 50 ml) and washed by saturated brine water. After drying over Na_2SO_4, filtering, and concentrating, the crude products were purified by column chromatography on silica gel (eluent: n-hexane to CH_2Cl_2) and provided **3** as yellow solid (6.1 g, 87%). ^{1}H-NMR (600 MHz, DMSO-*d*6) δ: 11.31 (s, 1H), 8.62 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.56 (t, *J* = 8.2, Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.29 (s, 1H), 2.78 (s, 3H). ^{13}C-NMR (150 MHz, DMSO-*d*6), δ: 205.00, 156.16, 129.97, 137.67, 134.24, 129.86, 127.15, 126.32, 124.35, 123.27, 111.43, 28.64. MS (HR ESI-TOF): m/z: calcd for $C_{12}H_{11}O_2^+$ $[M+H]^+$: 187.0754; found: 187.0751.

Additional Scheme, Table and Figures



Scheme S1 The ESIPT process of flavonoid dyes.



Scheme S2 Comparison of steric effects and rotation between **HOF** and **SHOF**.

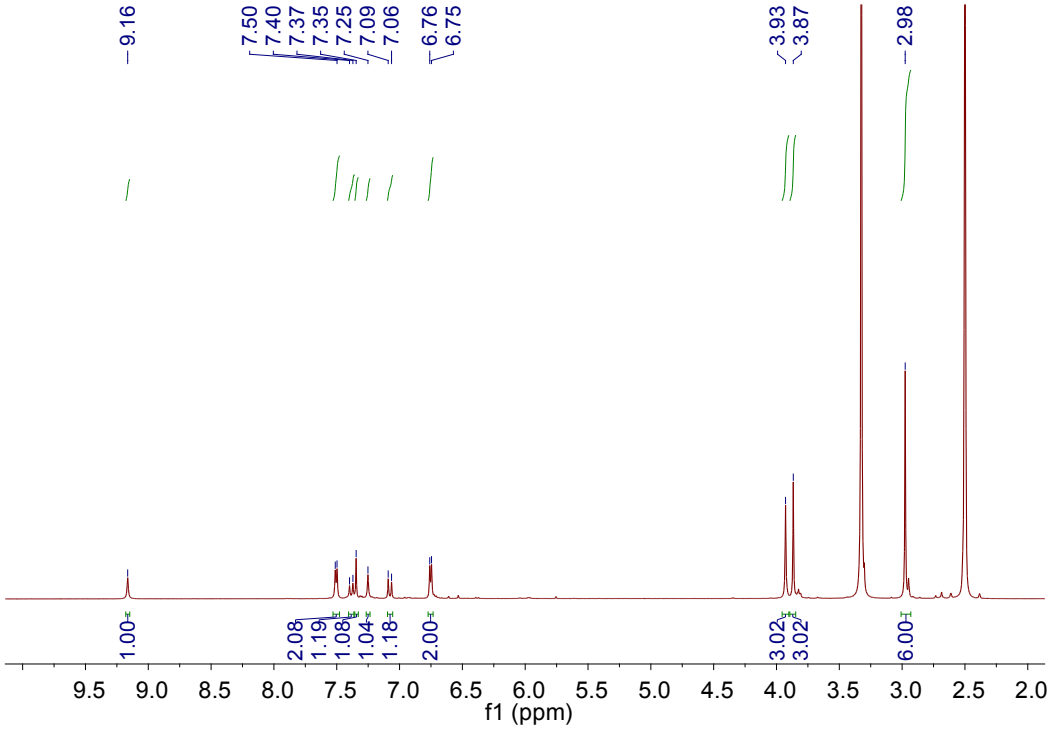


Fig. S1 ^{1}H NMR spectrum of **SHOF** in DMSO-*d*6.

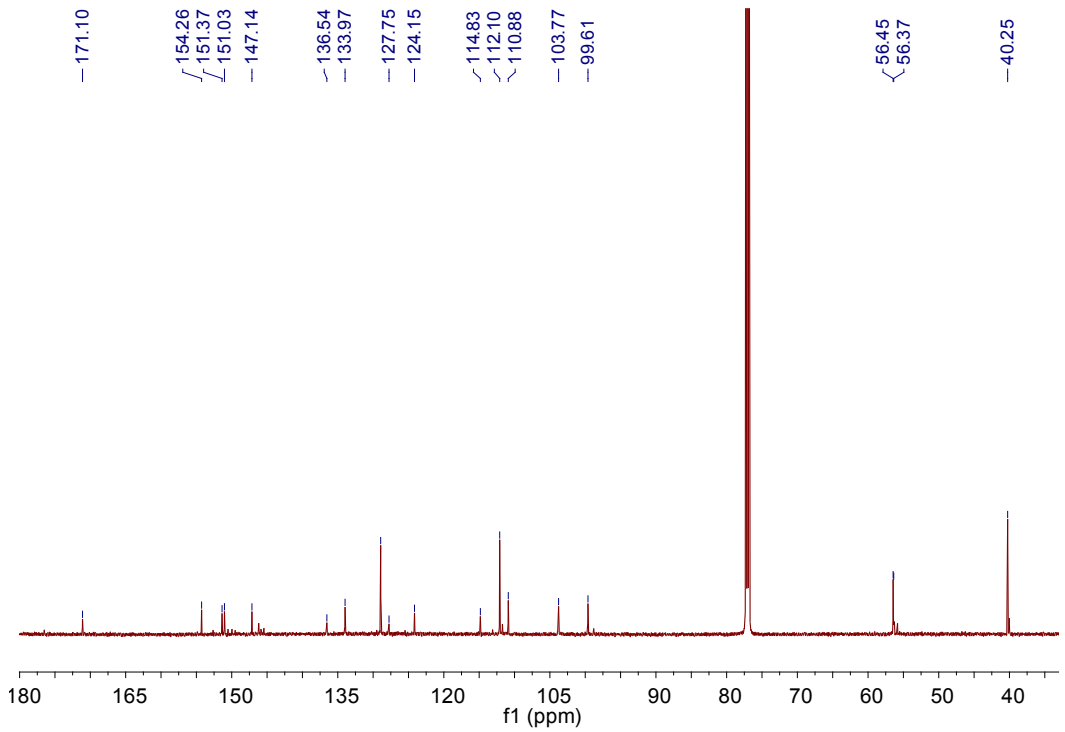


Fig. S2 ^{13}C NMR spectrum of **SHOF** in $CDCl_3$.

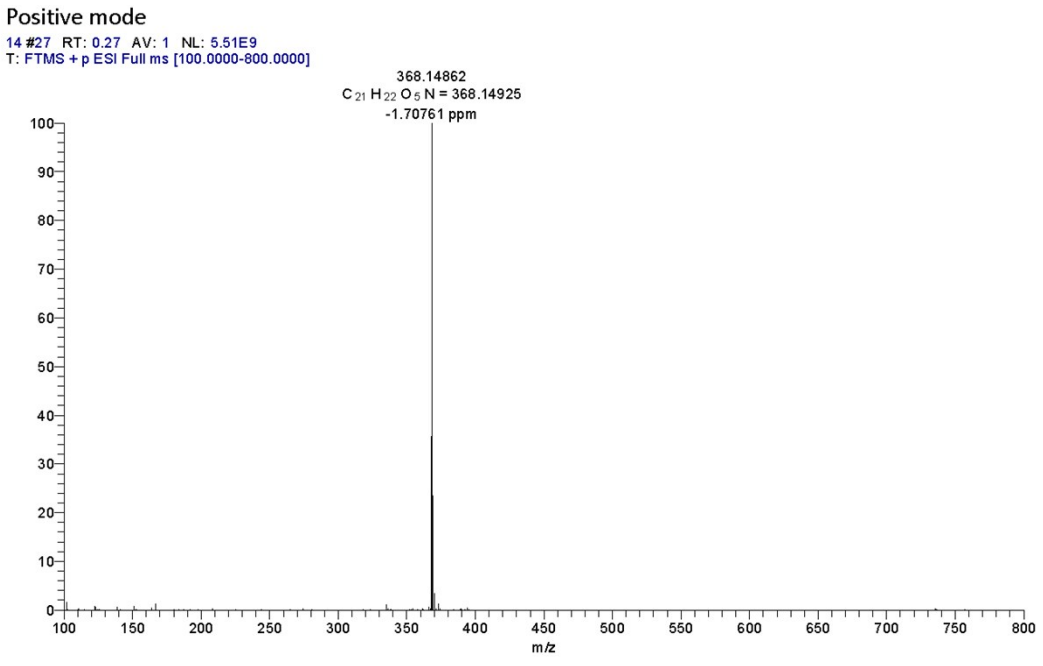


Fig. S3 HR ESI-TOF MS spectrum of **SHOF**.

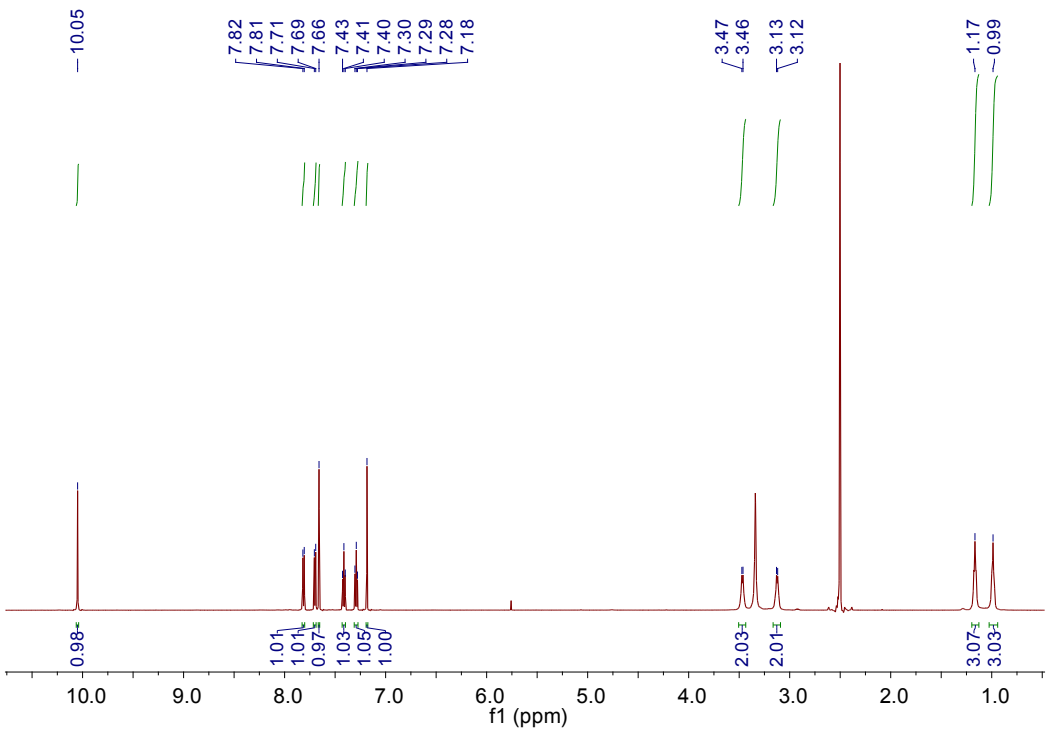


Fig. S4 ^{1}H NMR spectrum of **1** in DMSO-*d*6.

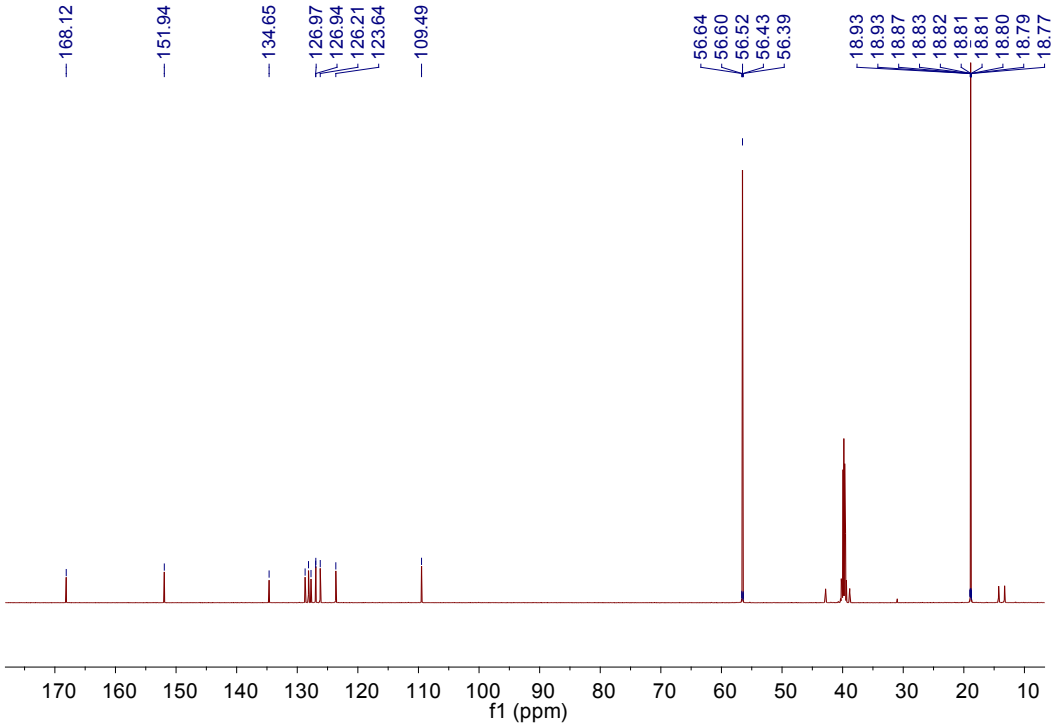


Fig. S5 ^{13}C NMR spectrum of **1** in DMSO-*d*6.

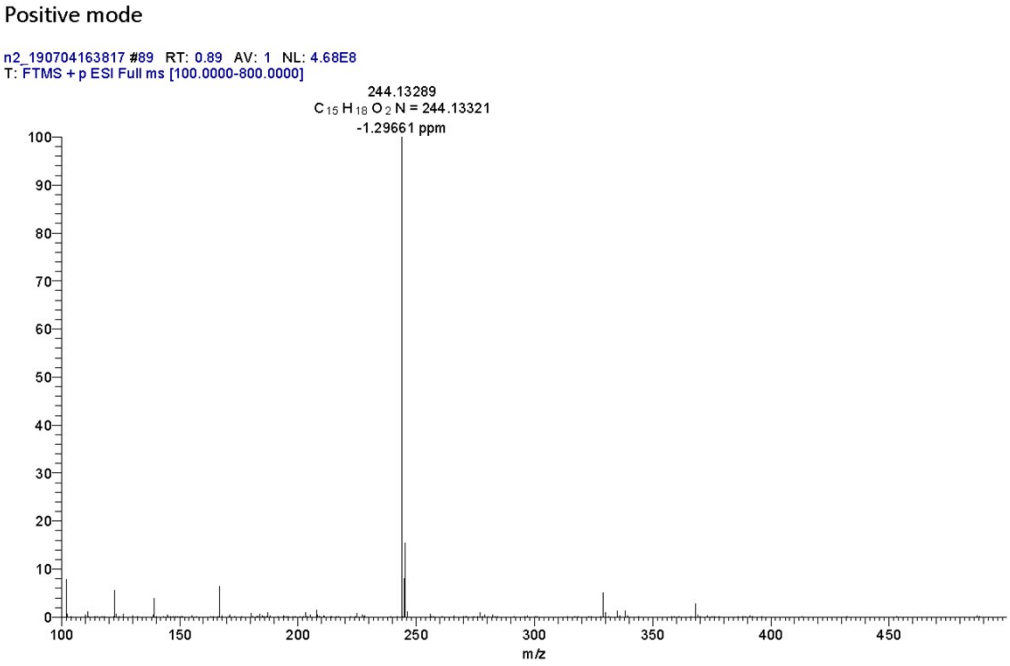


Fig. S6 HR ESI-TOF MS spectrum of **1**.

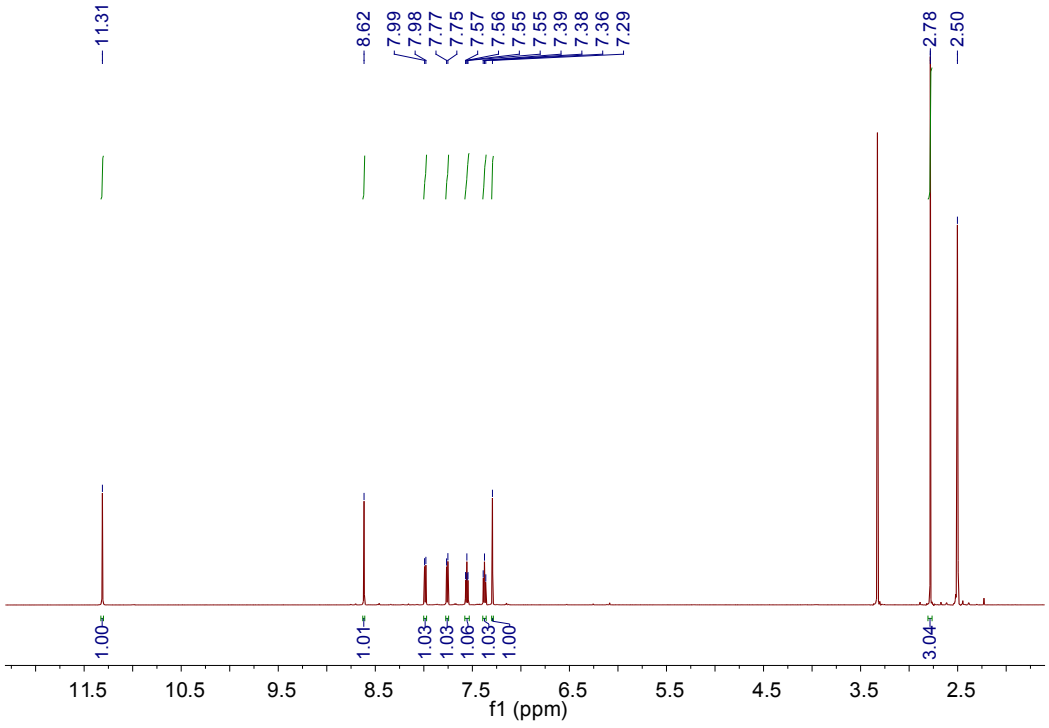


Fig. S7 ^{1}H NMR spectrum of **2** in DMSO-*d*6.

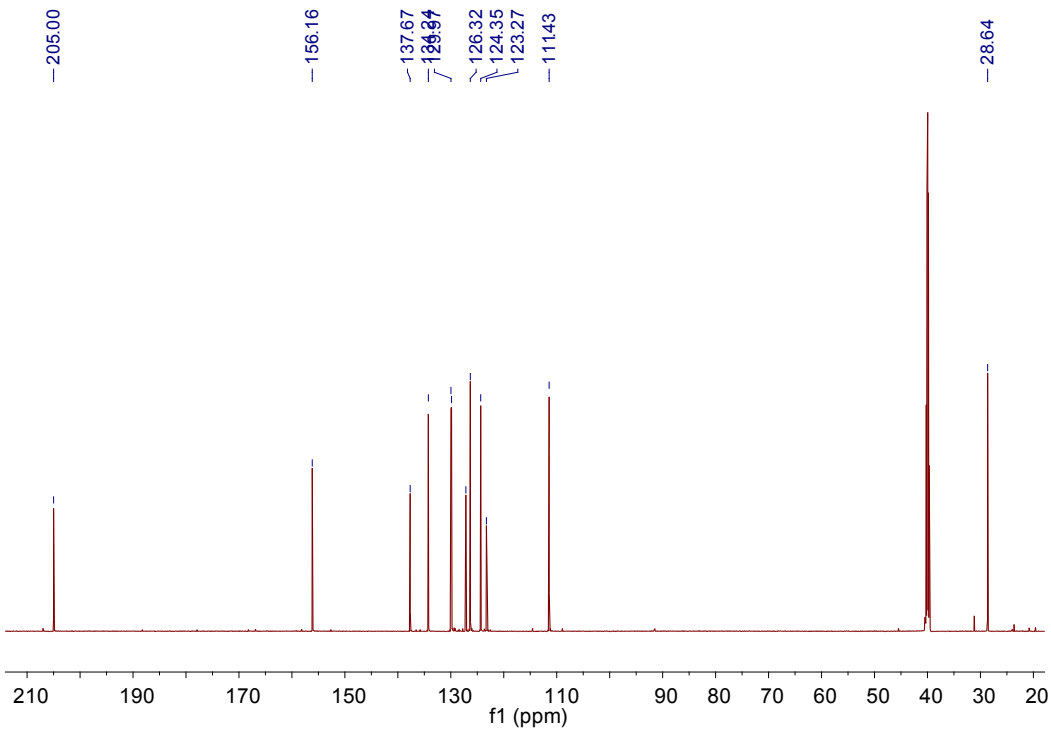


Fig. S8 ^{13}C NMR spectrum of **2** in DMSO-*d*6.

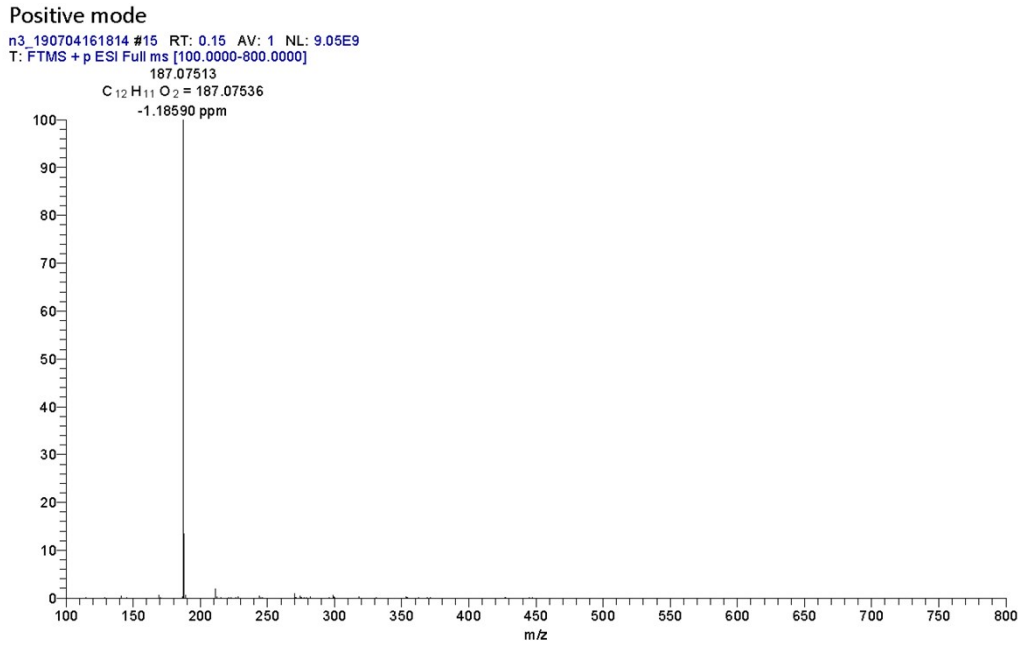


Fig. S9 HR ESI-TOF MS spectrum of **2**.

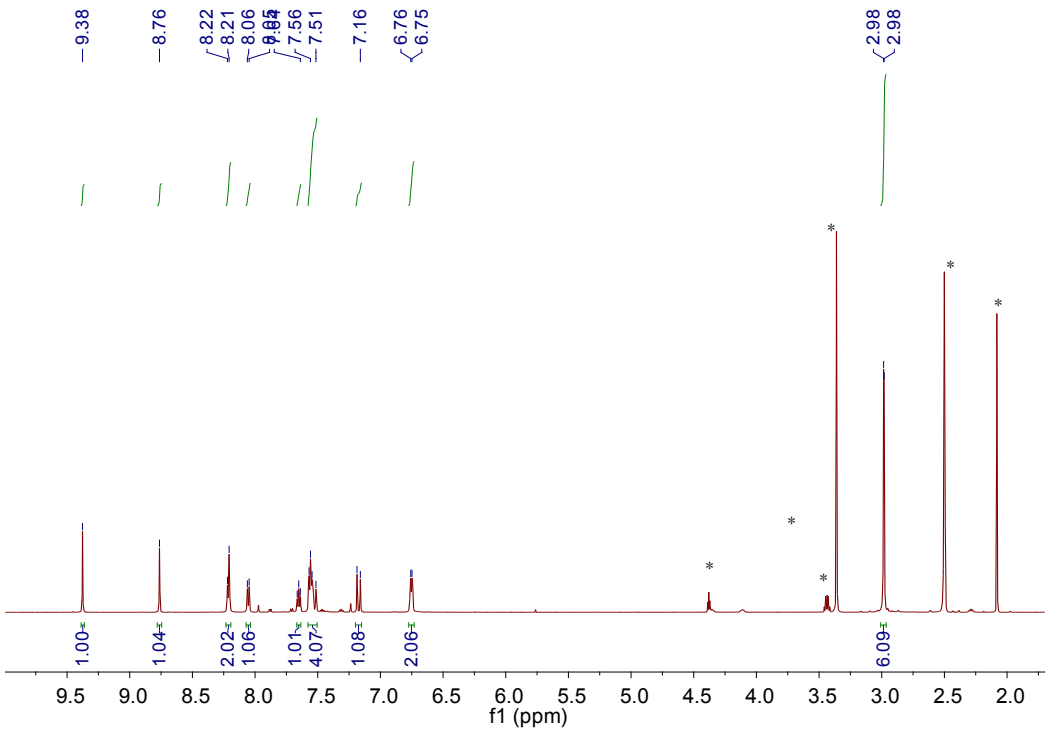


Fig. S10 ^{1}H NMR spectrum of **NSHOF** in DMSO-*d*6.

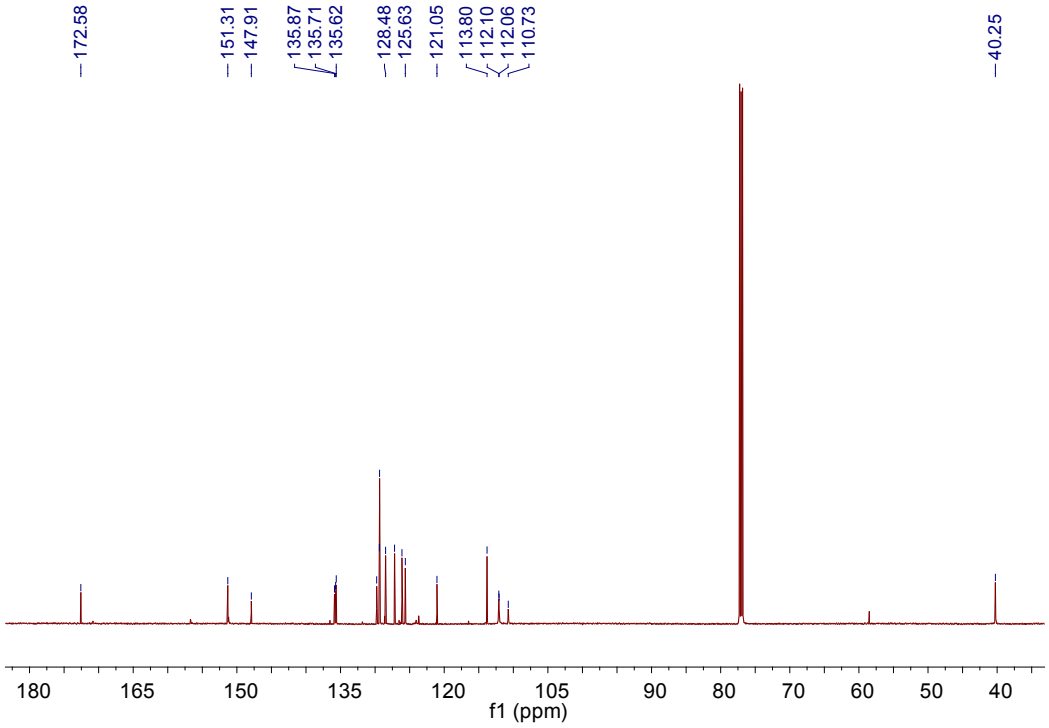


Fig. S11 ^{13}C NMR spectrum of **NSHOF** in $CDCl_3$.

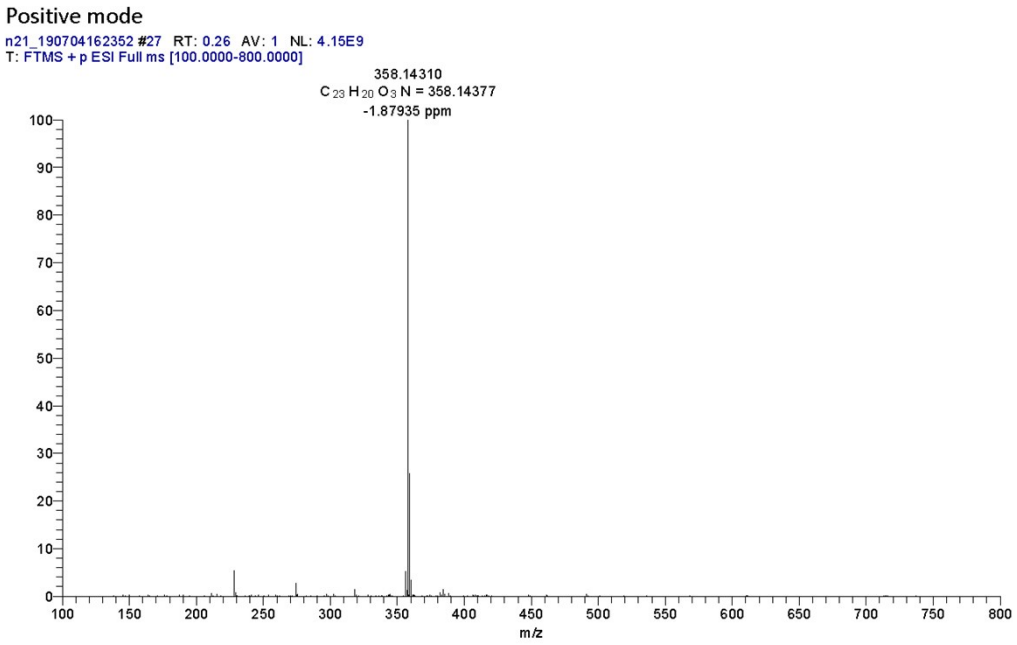


Fig. S12 HR ESI-TOF MS spectrum of **NSHOF**.

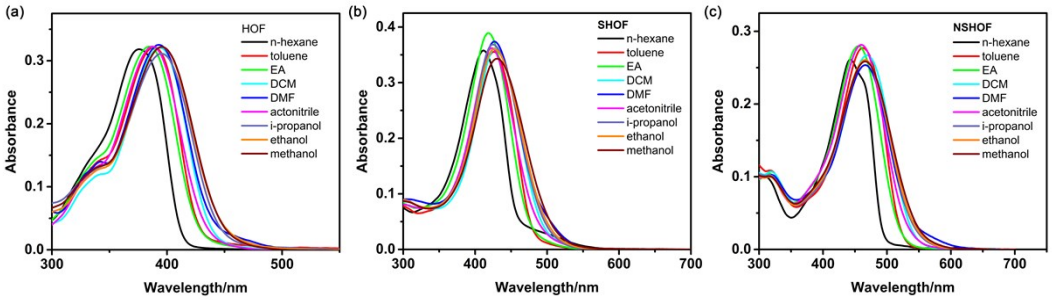


Fig. S13 The absorption spectra of **HOF**, **SHOF**, and **NSHOF** in organic solvents. [**HOF**] = [**SHOF**] = [**NSHOF**] = 10^{-5} M.

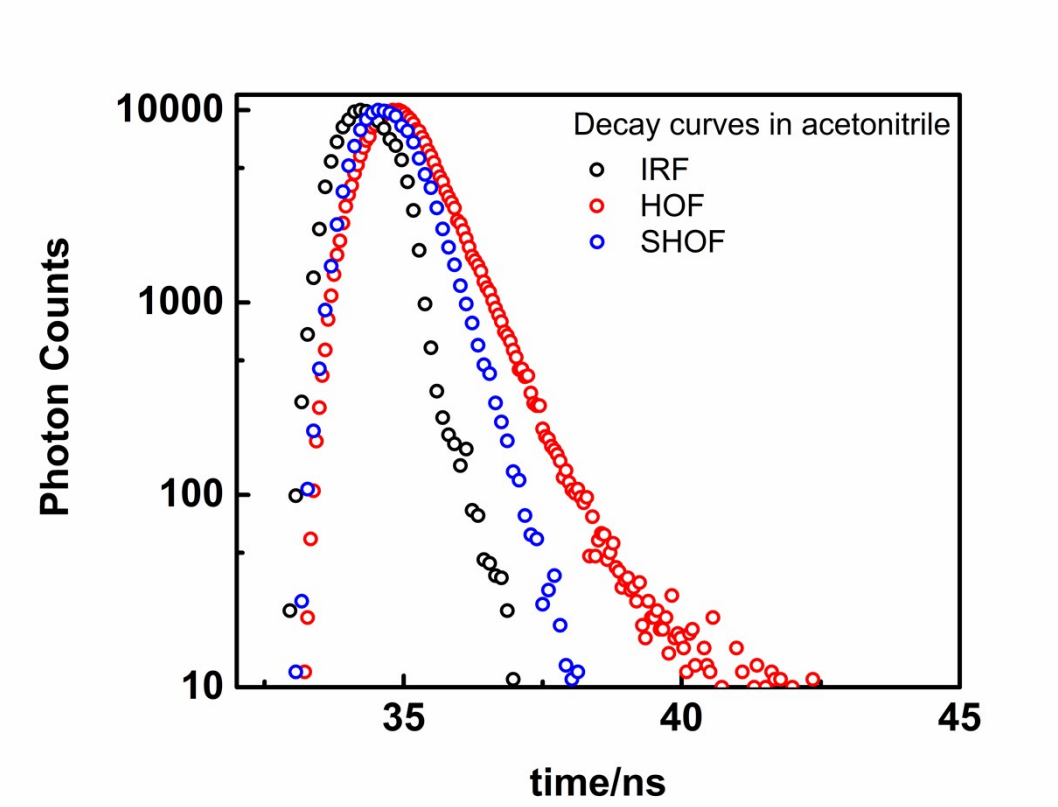


Fig. S14 Fluorescence decay curves of **HOF** and **SHOF** in acetonitrile. Excitation wavelength was 392 nm. IRF: instrument response function (prompt).

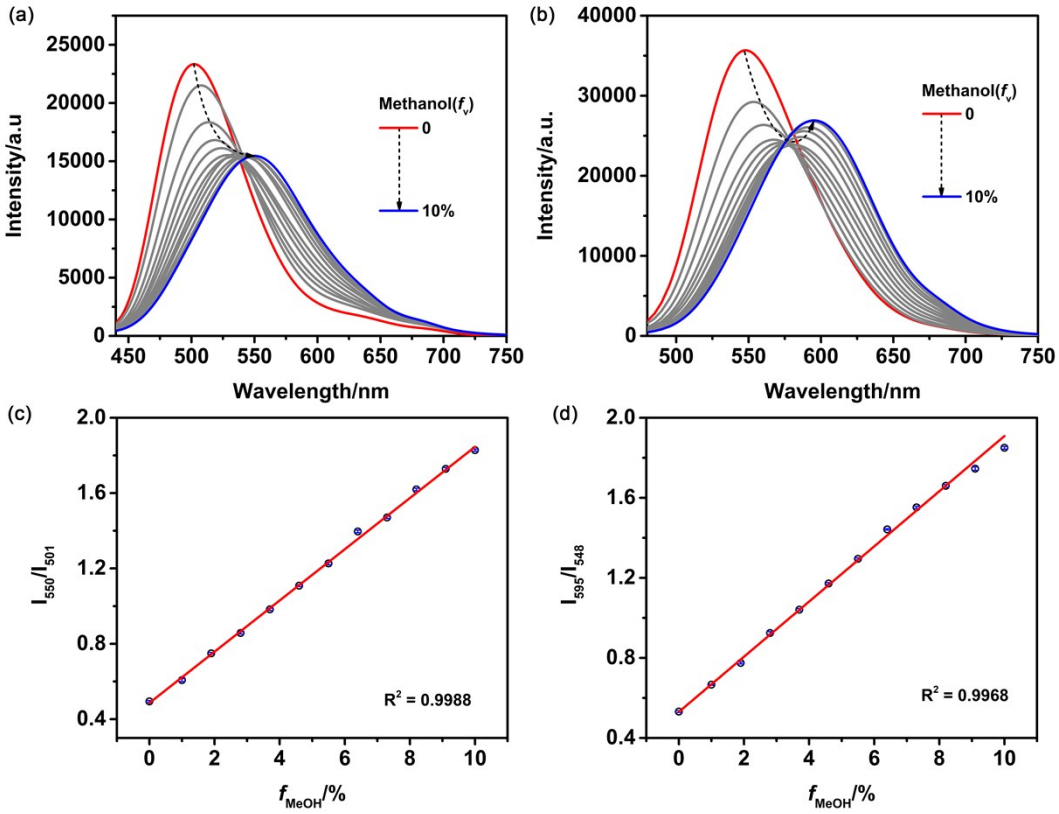


Fig. S15 (a, b) The fluorescent spectra of **SHOF** and **NSHOF** in biodiesel/methanol mixture (f_{MeOH}: 0 ~ 10%), The excitation wavelengths for **SHOF** and **NSHOF** were 420 nm and 460 nm, respectively. (c, d) The fluorescent intensity ratio of **SHOF** (I_{550}/I_{501}) and **NSHOF** (I_{595}/I_{548}) in biodiesel/methanol mixture (f_{MeOH}: 0 ~ 10%). [**SHOF**] = [**NSHOF**] = 10^{-5} M. Error bars were calculated from three parallel experiments.

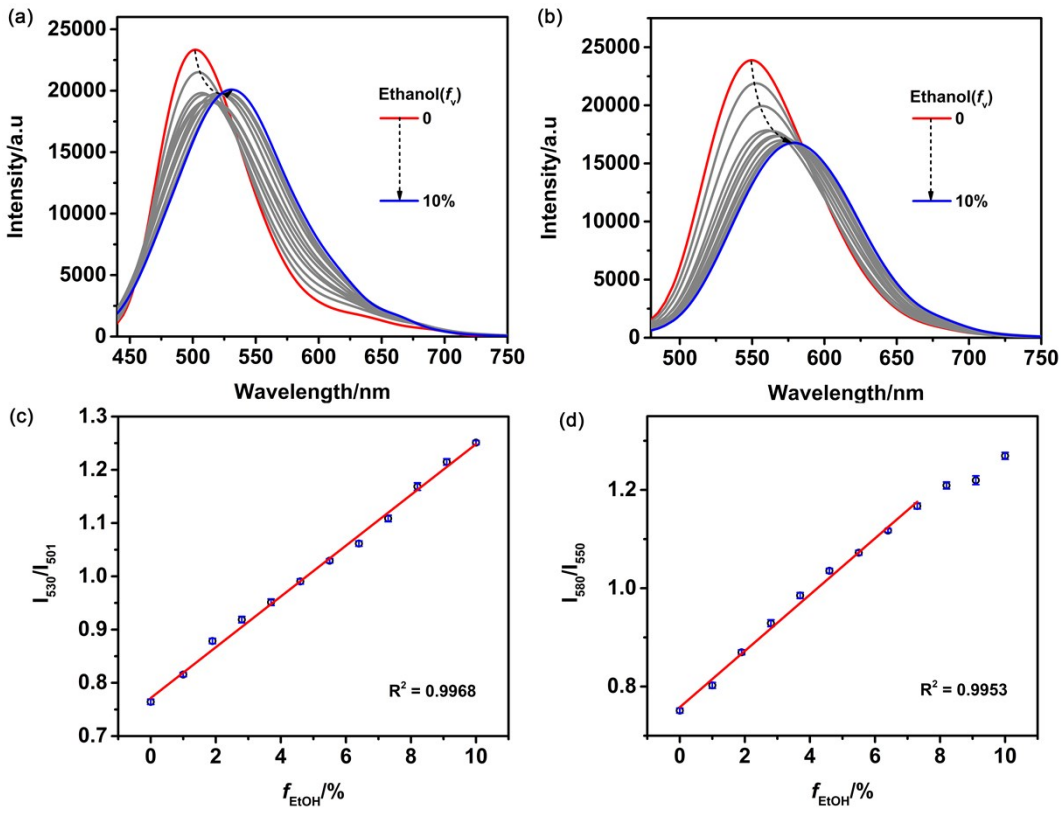


Fig. S16 (a, b) The fluorescent spectra of **SHOF** and **NSHOF** in biodiesel/ethanol mixture (f_{EtOH}: 0 ~ 10%), The excitation wavelengths for **SHOF** and **NSHOF** were 420 nm and 460 nm, respectively. (c, d) The fluorescent intensity ratio of **SHOF** (I_{530}/I_{501}) and **NSHOF** (I_{580}/I_{550}) in biodiesel/ethanol mixture (f_{EtOH}: 0 ~ 10%). [**SHOF**] = [**NSHOF**] = 10^{-5} M. Error bars were calculated from three parallel experiments.

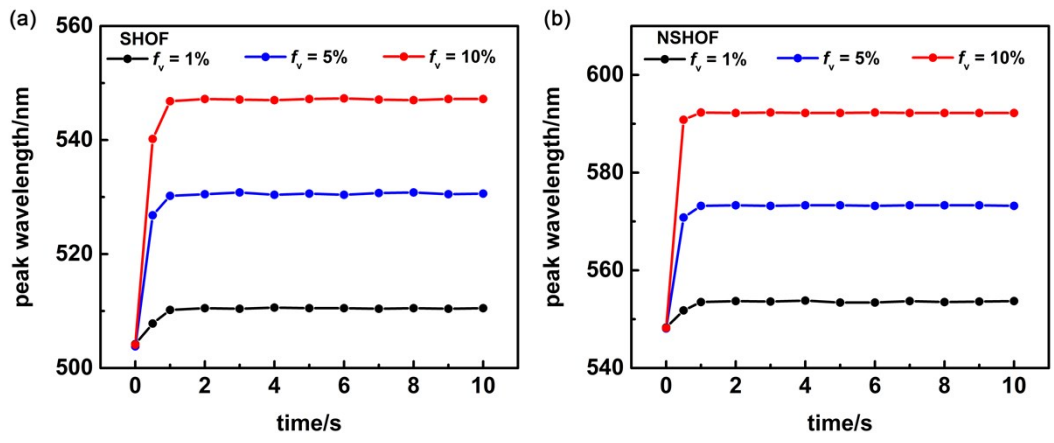


Fig. S17 The response time of **SHOF** (a) and **NSHOF** (b) in biodiesel with f_{MeOH} of 1% (black line), 5% (blue line), and 10% (red line) over a time scale from 0 to 10 min.

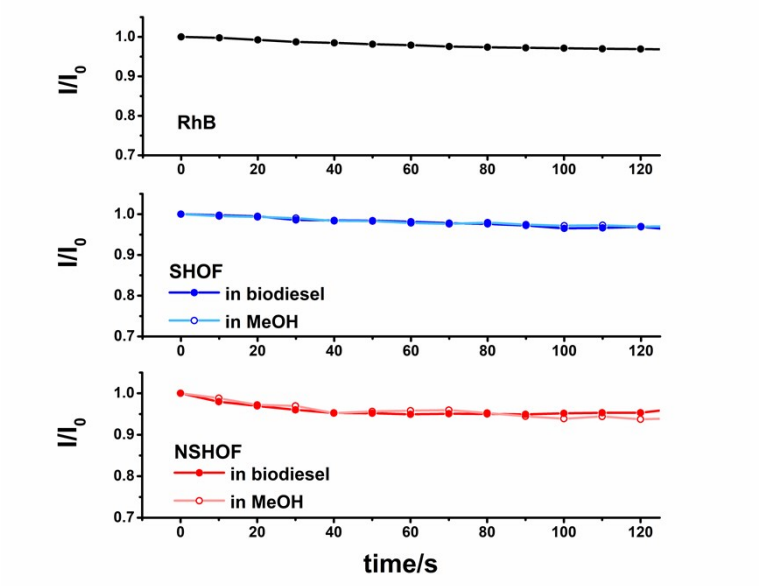


Fig. S18 The time-scan fluorescent spectra of rhodamine B (Ex/Em: 550/580) in DCM and **SHOF** (Ex/Em: 420/500), **NSHOF** (Ex/Em: 460/550) in biodiesel. The concentration of each sample was 10^{-5} M.

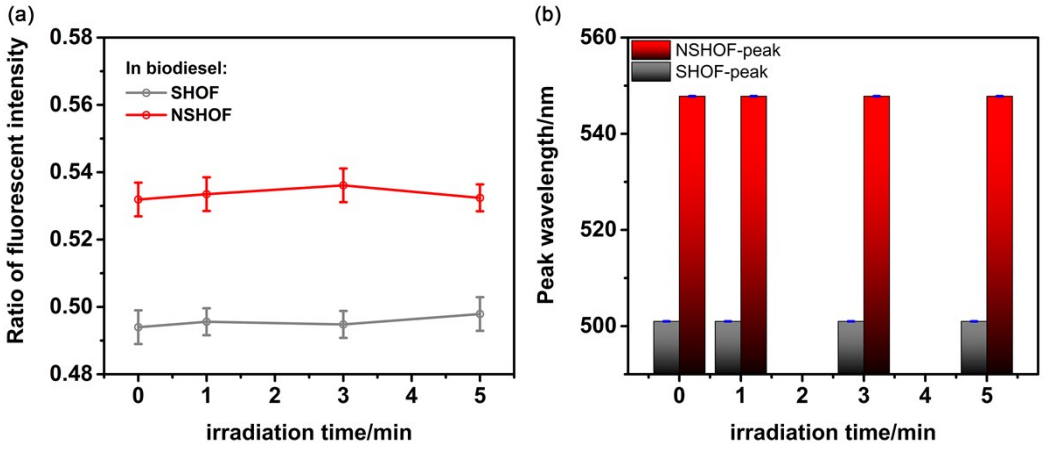


Fig. S19 The fluorescent ratio and peak wavelength of **SHOF** and **NSHOF** after continuous irradiation of UV light (~365 nm), c = 10^{-5} M. The excitation wavelengths

for **SHOF** and **NSHOF** were 420 nm and 460 nm, respectively. Error bars were calculated from three parallel experiments.

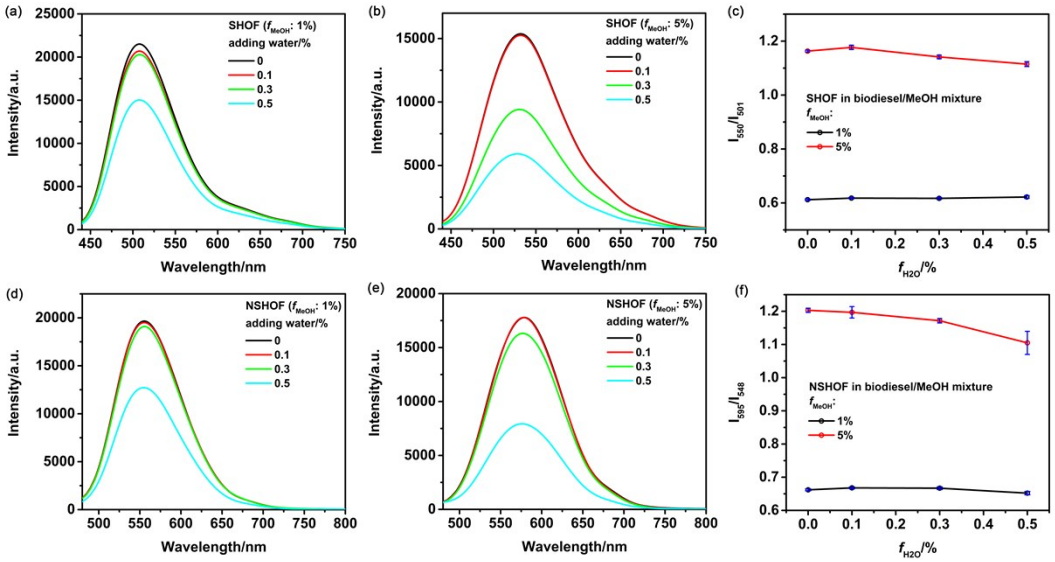


Fig. S20 The fluorescent spectra of **SHOF** (a, b) and **NSHOF** (d, e) in biodiesel/methanol mixture with water (f_{H2O}: 0, 0.1%, 0.3%, 0.5%). (c) and (f) The interference of water on the fluorescent ratios of **SHOF** (I_{550}/I_{501}) and **NSHOF** (I_{595}/I_{548}). The excitation wavelengths for **SHOF** and **NSHOF** were 420 nm and 460 nm, respectively. Error bars were calculated from three parallel experiments.

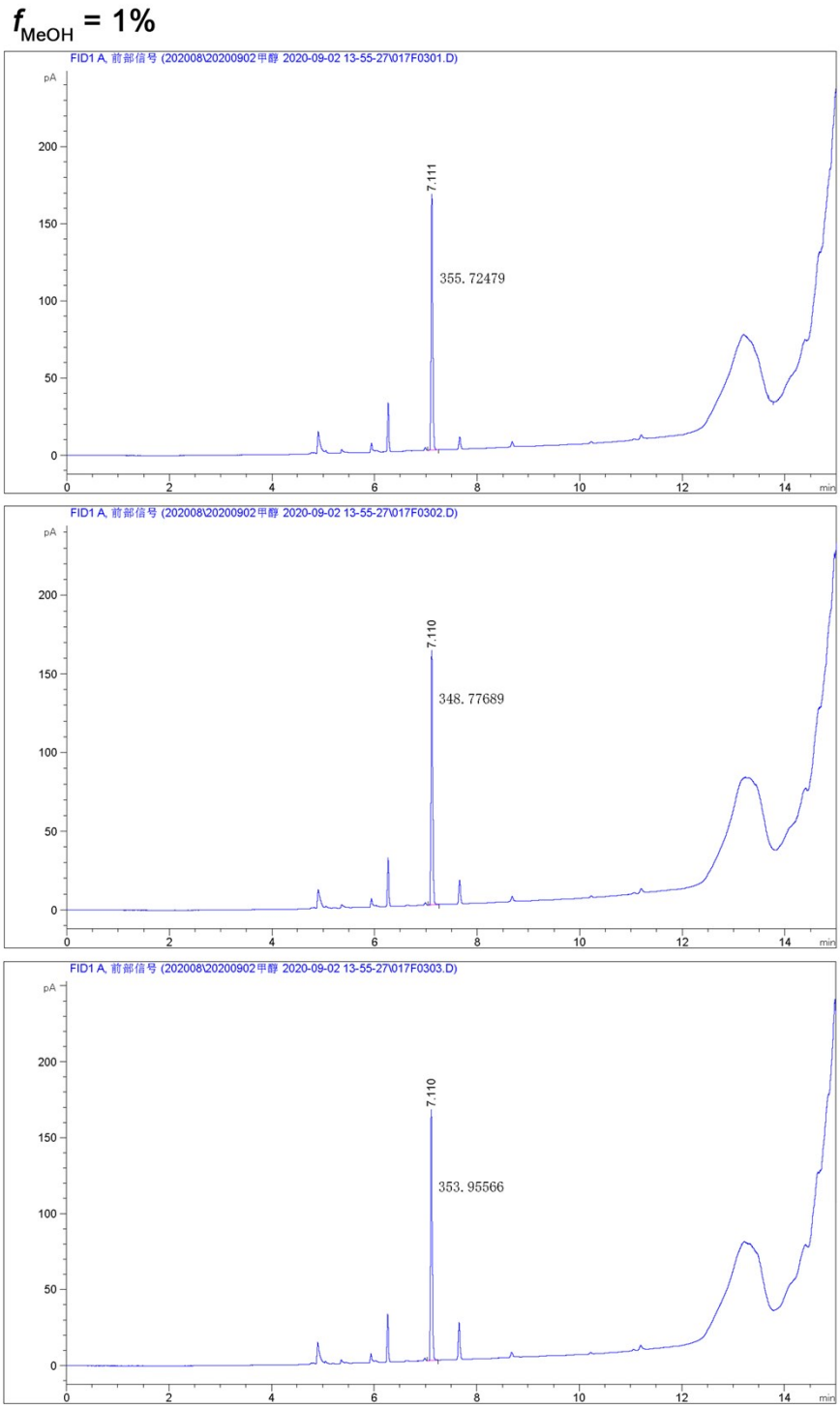


Fig. S21 Three parallel GC results of biodiesel sample with spiked methanol (f_{MeOH} = 1%).

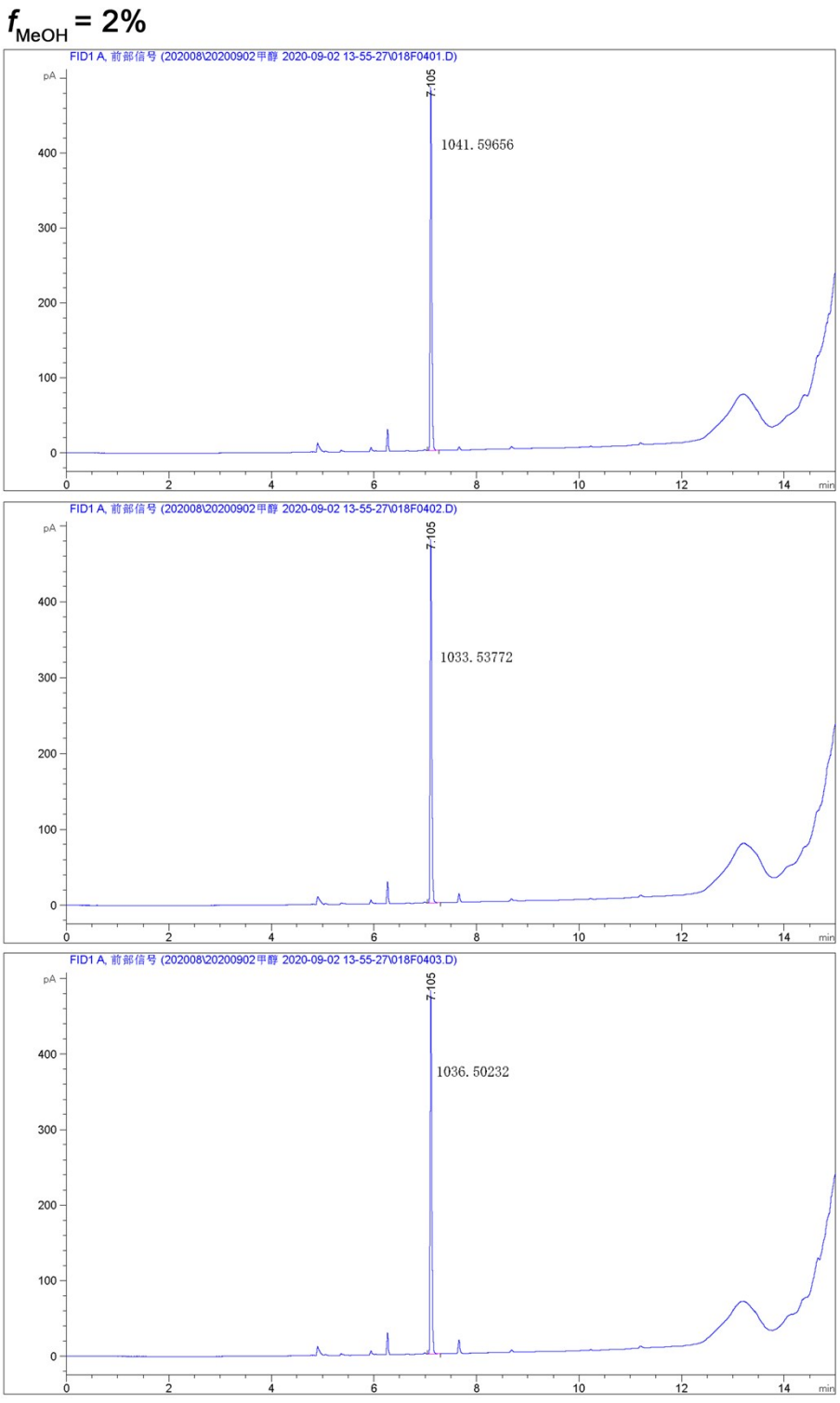


Fig. S22 Three parallel GC results of biodiesel sample with spiked methanol (f_{MeOH} = 2%).

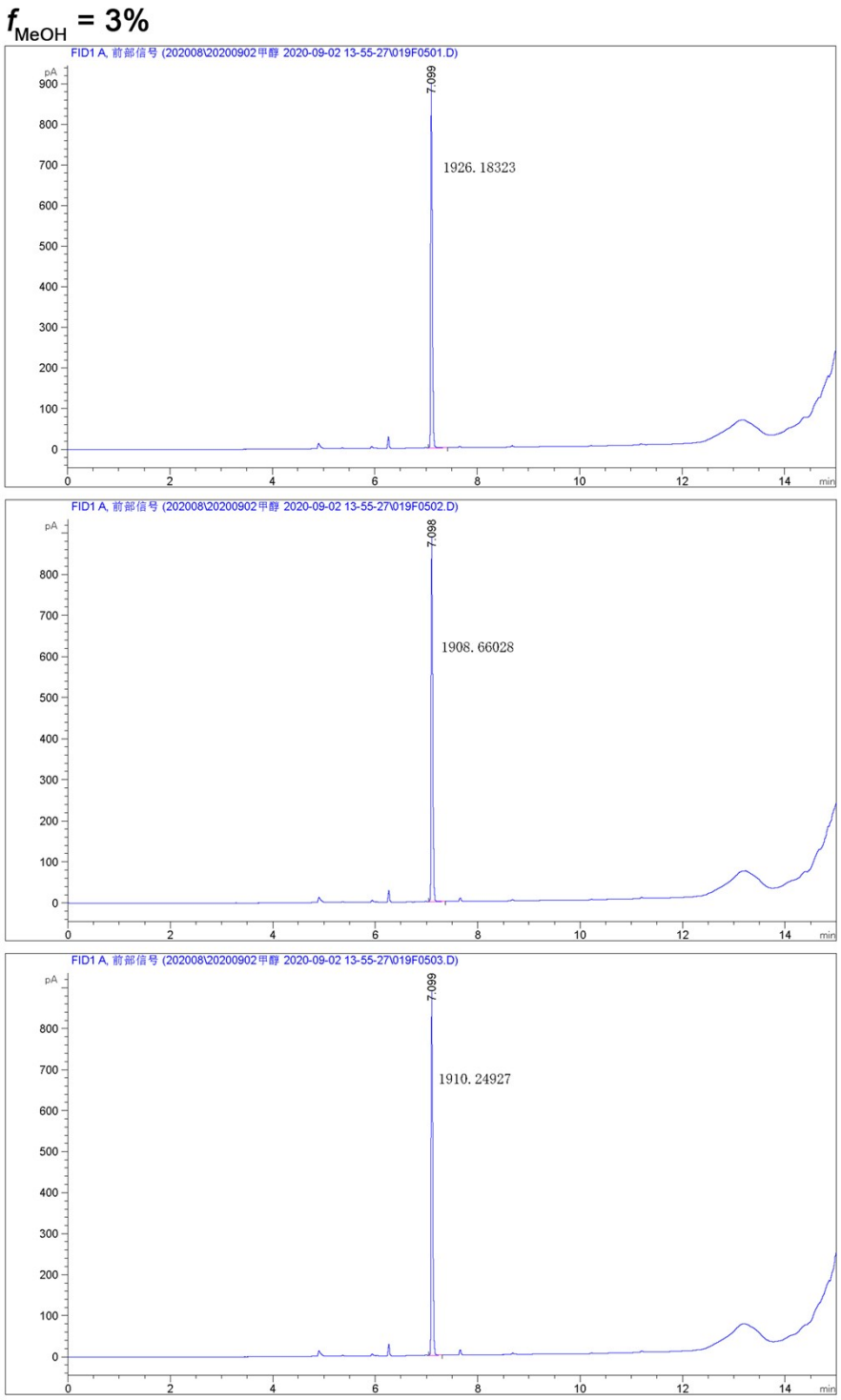


Fig. S23 Three parallel GC results of biodiesel sample with spiked methanol (f_{MeOH} = 3%).

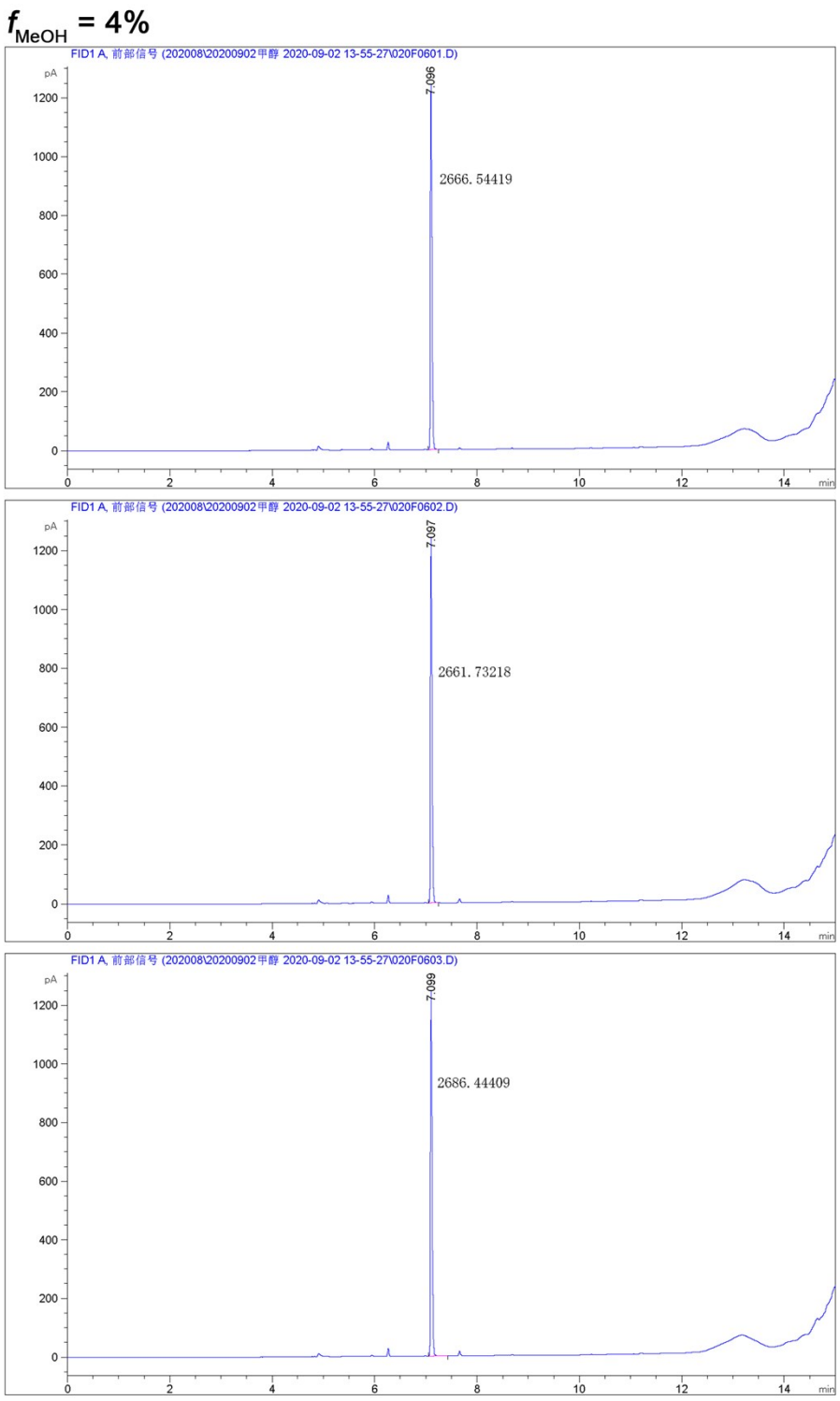


Fig. S24 Three parallel GC results of biodiesel sample with spiked methanol (f_{MeOH} = 4%).

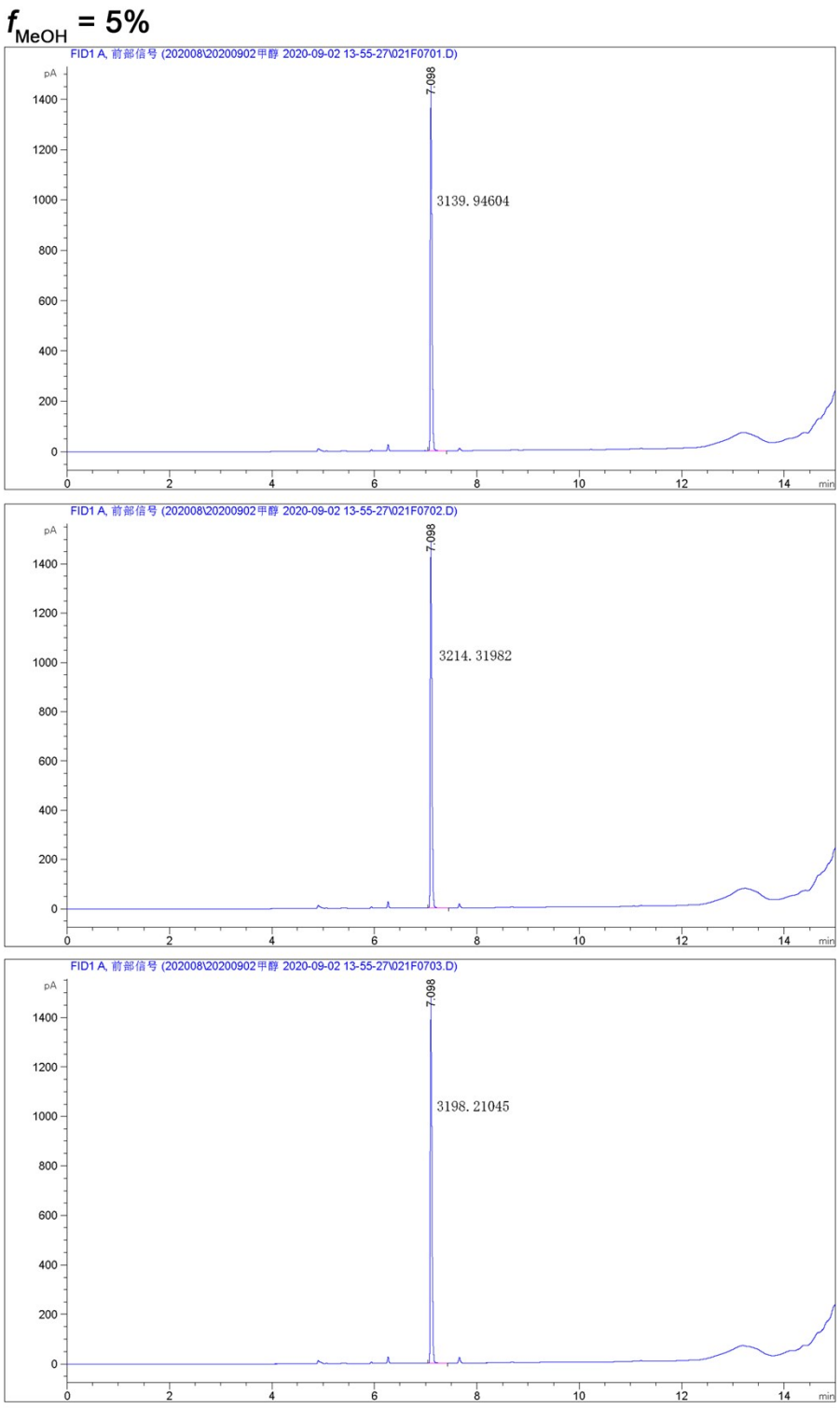


Fig. S25 Three parallel GC results of biodiesel sample with spiked methanol (f_{MeOH} = 5%).

Table S1 The radiation (k_r) and non-radiation (k_{nr}) rates of **HOF** and **SHOF** in acetonitrile.

	τ/ns	Φ_F	k/ns^{-1}	k_r/ns^{-1}	k_{nr}/ns^{-1}
HOF	0.56	0.15	1.79	0.27	1.52
SHOF	0.13	0.05	7.69	0.38	7.31

Table S2 The color information of **HOF**, **SHOF**, and **NSHOF** in biodiesel with varying methanol content (f_v).

	f_v **(%)**	R	G	B	L*	a*	b*	ΔE* (between f_n and f_{n-1}, n: 1~10)
HOF	0	218	216	38	84.5	-12.6	77.5	-
	1	218	222	40	86.1	-15.4	78.4	3.3
	2	218	223	47	86.3	-15.7	76.9	1.5
	3	214	222	56	85.8	-16.6	73.8	3.3
	4	209	219	61	84.6	-17.1	71	3.1
	5	204	216	65	83.4	-17.7	68.4	2.9
SHOF	0	35	215	171	77	-52.5	35.7	-
	1	80	221	139	79.1	-53.5	28.7	19.8
	2	125	223	114	81	-46	43.7	16.9
	3	170	219	113	82.2	-29.4	46.3	16.8
	4	193	226	84	85.5	-25.7	63	17.4
	5	184	212	60	80.8	-24.1	67	6.4
NSHOF	0	114	162	6	61.4	-31.3	61.2	-
	1	163	204	1	76.9	-30.1	75.1	20.9
	2	172	192	1	74.2	-21.2	73.4	9.5
	3	208	195	1	78	-7.3	77.6	15

	4	190	146	1	63.4	9.4	66.9	24.6
	5	184	99	1	51.4	31.3	59.3	26.1

Table S3 Comparison of the GC method and two fluorescent probes for methanol in biodiesel.

Sample[a]	Spiked methanol	GC method (mean±SD)[b]	**SHOF** (mean±SD)[b]	Recovery	RSD[c]	**NSHOF** (mean±SD)[b]	Recovery	RSD[c]
	/%	/%	/%	/%	/%	/%	/%	/%
Biodiesel samples	1	0.99±0.005	0.90±0.03	91	3.3	0.88±0.04	88	4.5
	2	1.90±0.005	1.89±0.07	95	3.7	1.90±0.05	95	2.6
	3	3.00±0.001	2.92±0.02	97	0.7	3.08±0.05	102	1.6
	4	4.00±0.017	4.09±0.01	102	0.2	3.94±0.03	99	0.8
	5	4.70±0.012	4.87±0.01	97	0.2	5.10±0.02	102	0.4

NOTE: [a] The samples were prepared artificially by adding methanol (1 ~ 5%) into biodiesel samples; [b] mean of three parallel experiments, SD = standard deviation; Δf is the polarizability factor in Lippert-Mataga equation; [c] Relative standard deviation of mean recovery (RSD (%) = (SD/mean) × 100).