# Supporting Information

# A colorimetric and fluorometric dual-modal sensor for methanol

# based on a functionalized pentacenequinone derivative

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### Materials and instrumentation

Starting materials and reagents were purchased from Tokyo Kasei Kogyo (TCI: Tokyo, Japan), AR grade solvents of MeOH, EtOH, acetone, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, 1,4-dioxane, DMF, CH<sub>3</sub>CN, dimethylsulfoxide (DMSO), tetrahydrofuran (THF), ethyl acetate (EA), ethylene glycol, *n*-propyl alcohol, *iso*-propanol, *n*-butyl alcohol, *tert*-butyl alcohol, and *iso*-amyl alcohol were purchased from Alfa-Aesar, and used without further purification. The reactions were carried out in ovendried glasswares with a magnetic stirring. IR spectra were obtained with a Frontier Mid-IR FTIR spectrometer. NMR spectra were recorded on a Bruker spectrometer at 400 (<sup>1</sup>H NMR) MHz and 100 (<sup>13</sup>C NMR) MHz. Chemical shifts (d values) were reported in ppm down field from internal Me<sub>4</sub>Si (<sup>1</sup>H and <sup>13</sup>C NMR). High resolution mass spectra (HRMS) were acquired on an Agilent 6510 Q-TOF LC/MS instrument (Agilent Technologies, Palo Alto, CA) equipped with an electrospray ionization (ESI) source. Melting points were recorded on a Boethius Block apparatus. All absorption spectra were recorded using a Shimadzu UV-2550 UV/Vis spectrophotometer with 1cm quartz cell. In a similar manner, fluorescence spectra were recorded on a Hitachi F-4600 spectrofluorophotometer with a 1 cm quartz cell.

### Synthesis and Compound Characterizations

#### The preparation of ZR.

To a 50 mL flask, 2-(4-(N,N-dibutylamino)-2-hydroxy-benzoyl)benzoic acid (0.369 g, 1 mmol) and 1,4,9,10-anthracenetetrol (0.242 g, 1.1 mmol) were mixed in methanesulfuric acid (1 mL) and heated at 85 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into stirred ice water. The aqueous phase was adjusted to ca. pH 7.0 with Na<sub>2</sub>CO<sub>3</sub>, and then extracted with dichloromethane (30 mL  $\times$  3). The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The blue residue was purified by silica gel column chromatography (DCM/petroleum ether, 100/2-100/10, v/v) to yield the product ZR as blue powder in 65 % yield (0.397 g), m.p. 220-224 °C. IR (KBr): 2966, 2928, 2871, 1621, 1589, 1523, 1480, 1450, 1429, 1386, 1320, 1271, 1121, 1059, 739, and 636 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): 15.82 (s, 1H), 14.18 (s, 1H), 8.46 (d, J = 8.0 Hz, 1H), 8.42 (d, J = 7.8 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 6.8 Hz, 1H), 7.81 (d, J = 9.6 Hz, 1H), 7.63 (t, J = 3.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 6.68 (s, 1H), 6.47 (d, J = 7.2 Hz, 1H), 3.33 (t, J = 7.6 Hz, 4H), 1.69-1.61 (m, 4H), 1.48-1.38 (m, 4H), 1.02 (t, J = 7.2 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm) 185.17, 177.14, 164.06, 161.20, 159.30, 153.37, 152.37, 136.07, 131.87, 131.79, 131.16, 130.46, 130.30, 127.86, 127.44, 127.39, 127.36, 126.64, 124.95, 124.91, 123.39, 109.40, 109.36, 109.28, 107.45, 107.36, 106.18, 50.76, 29.55, 20.39, 14.06.

#### The preparation of ZR1.

The product **ZR** (0.397 g, 0.67 mmol) was refluxed in 30 mL anhydrous ethanol solution with 8 mL concentrated sulfuric acid. During the refluxing, the blue solution was changed to red. After refluxing for 24 h, the red reaction mixture was poured onto ice under vigorous stirring. The pH of the aqueous phase was adjusted to ca. 7.0 with Na<sub>2</sub>CO<sub>3</sub>. Then, the reaction mixture was stirred for 20 min and subsequently extracted with dichloromethane (30 mL × 3). The crude product was purified by silica gel column chromatography (petroleum ether /DCM, 100/10-100/25, v/v) to give

**ZR1** in 59 % yield (0.235 g), m.p. 228-230 °C. HRMS: m/z  $[M + H]^+ = 576.2386$ ; Calcd: 576.2381; IR (KBr): 2963, 2929, 2869, 1629, 1585, 1514, 1467, 1429, 1385, 1255, 1184, 1104, 1061, 1027, 822, 762, 655, and 587 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): 15.20 (s, 1H), 14.71 (s, 1H), 13.95 (s, 1H), 8.46 (t, J = 6.0 Hz, 2H), 8.41 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 7.64-7.58 (m, 5H), 6.74 (d, J = 8.0 Hz, 1H), 6.43 (d, J = 2.0 Hz, 1H), 6.37 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 3.36 (t, J = 7.6 Hz, 4H), 1.75-1.67 (m, 4H), 1.47-1.38 (m, 4H), 1.02 (t, J = 7.2 Hz, 6H); <sup>13</sup>C NMR (DMF-d<sub>7</sub>, 100 MHz, ppm) 191.1, 188.1, 164.4, 163.6, 160.4, 158.1, 157.0, 150.5, 139.8, 136.5, 132.9, 132.7, 131.9, 131.1, 130.5, 130.4, 128.3, 127.4, 125.9, 125.8, 125.3, 114.8, 111.5, 108.9, 108.0, 104.7, 100.3, 51.8, 30.9, 21.4, 14.9.

#### Solutions for optical measurements

Stock solutions of **ZR1** (5 mM) was prepared in DMSO. Test solutions were prepared by placing appropriate volume (6  $\mu$ L) of the stock solution into a 5 mL vial, adding an appropriate aliquot of each solvent to dilute the solution to 3 mL. After equilibration for 30 min, the data were collected at room temperature.

For the colorimetric and fluorometric titrations, the spectra were measured immediately after adding incremental amounts of methanol to the ethanol solutions of **ZR1**.

#### Preparation the sample of 'Red Star Erguotou'.

Commercially available Red Star Erguotou (200 mL, 56% vol) was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> (50 g × 3). After removal of Na<sub>2</sub>SO<sub>4</sub> by filtration, the filtrate was distilled to remove of the residual Na<sub>2</sub>SO<sub>4</sub> in the sample. Then, the water content in the sample was determined by using the method by the China GB/T10345-2007 standard. The water content in this pretreated sample is 8  $\pm$  0.05%. Before measurements, 3 mL solution in a quartz cell (1×1 cm) was prepared by adding an appropriate aliquot of the stock solutions of **ZR1** and the treated 'Red Star Erguotou', and then the UV-Vis absorption and fluorescence spectra were recorded immediately.

#### Preparation the sample of mimic methanol-containing gasolines.

The components of the mimic methanol-containing gasolines are petroleum ether (50%) and alcohols (50%), and alcohols were ethanol, and ethanol containing 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% of methanol. Before measurements, 3 mL solution in a quartz cell ( $1 \times 1$  cm) was prepared by adding an appropriate aliquot of the stock solutions of **ZR1** and the mimic methanol-containing gasolines, and then the ultraviolet absorption and fluorescence spectra were measured immediately.

#### pH effect

The pH values of ethanol containing water 5% vol. were adjusted by diluted HCl (0.1 M). And then 3 mL solution in a quartz cell (1×1 cm) was prepared by adding an appropriate aliquot of the stock solutions of **ZR1** and ethanol with different pH value. The ultraviolet absorption and fluorescence spectra of the solutions were measured. And then methanol (500  $\mu$ L) was introduced and the ultraviolet absorption and fluorescence spectra were measured immediately after the addition of methanol.

#### Determination of the Fluorescence Quantum Yield.

Fluorescence quantum yield ( $\Phi_1$ ) was determined by using rhodamine B ( $\Phi_1 = 0.71$ , in ethanol)<sup>1</sup> as the fluorescence standard. The quantum yield was calculated using the following equation.

$$\Phi_1 = \Phi_B \times \frac{Abs_B \times F_1 \times \lambda_{exB} \times \eta_1}{Abs_1 \times F_B \times \lambda_{ex1} \times \eta_B}$$

Where  $\Phi_1$  is the fluorescence quantum yield, A is the absorbance at the excitation wavelength, F is the area under the corrected emission curve, and  $\eta$  is the refractive index of the solvent used. Subscripts 1 and B refer to the unknown and to the standard, respectively.

<sup>&</sup>lt;sup>1</sup> T.Karstens, K. Kobs, J. Phys. Chem. 1980, 84, 1871.

Solvents	$\lambda_{abs} (nm)$	$\epsilon (M^{-1}cm^{-1})$	Φ	$\lambda_{em}(nm)$
acetone	494/518	22900/21600	0.1105	566/608
Dioxane	494/517	23800/21700	0.1605	572/612
CHCl <sub>3</sub>	500/523	22900/20500	0.1501	570/612
DCM	498/522	18500/16600	0.1665	570/609
DMF	497/522	25284/24338	0.1257	573/614
DMSO	500/524	21600/21100	0.1185	586/610
EtOAc	494/517	23300/21300	0.1250	565/608
EtOH	494/518	25000/23500	0.1121	565/609
MeCN	494/516	24100/22000	0.1221	566/608
MeOH	528/566	24300/26100	0.0510	606
THF	496/520	25700/23900	0.1185	569/611
H <sub>2</sub> O	500/542	10900/8200	0.0277	562

Table S1. Photophysical properties of ZR1 in different solvents

Table S2. Photophysical properties of ZR1 in different alcohols

Solvents	$\lambda_{abs}$ (nm)	$\epsilon (M^{-1} cm^{-1})$	Φ	$\lambda_{em}$ (nm)
Tert-butanol	494/518	22900/21600	0.1859	563/606
Isopropanol	494/517	23800/21700	0.1300	563/606
Propanol	500/523	22900/20500	0.1554	565/608
N-butanol	498/522	18500/16600	0.1895	566/609
EtOH	494/518	25000/23500	0.1121	565/609
MeOH	528/566	24300/26100	0.0510	606



**Figure S1.** a) Ultraviolet absorption and b) fluorescence intensities of **ZR1** (10  $\mu$ M) in ethanol in the presence and absence of MeOH (500  $\mu$ L) under different pH conditions.



**Figure S2.** Time-dependent IR spectra of **ZR1** in DMSO in the presence and absence of methanol. a) Overlapped spectra of **ZR1** in DMSO after addition of methanol. Insets of 1a): Plots of the carbonyl signal at 1655 cm<sup>-1</sup> versus time; b) Zoom in of a) between 1100-1800 cm<sup>-1</sup>, which showed the time-dependent changes of the carbonyl signal after the addition of methanol.



Figure S3. IR spectra (KBr) of ZR a) and ZR1 b).



**Fig. S4.** Methanol concentration-dependent response curve: emission ratio data extracted from Fig. 4b. The solid line is based on a sigmoidal curve fitting.<sup>2</sup>



**Fig. S5.** The fluorescence intensity change ( $\Delta F = F - F_0$ ) versus [MeOH]. The detection limit was calculated with the following equation<sup>3</sup>: Detection limit =  $3\sigma/k$ , where  $\sigma$  is the standard deviation of fluorescence intensity of **ZR1**, respectively; k is the slop between the fluorescence intensity change versus MeOH concentration (k = 101.84369). The fluorescence emission spectrum of probe **ZR1** was measured by eleven times and the standard deviation of blank measurement was found to be 1.279431, the detection limit is 0.038% (volume ratio).



**Fig. S6** Time-dependent fluorescence intensity at 564 nm of **ZR1** (10  $\mu$ M) in ethanol (red), and those recorded immediately after the addition of 15% methanol in ethanol (black).  $\lambda_{ex} = 500$  nm, slit = 10 nm, 10 nm.

<sup>&</sup>lt;sup>2</sup> K, Takano, S, Sasaki and K, Suzuki, Analyst, 2010, 135, 2334

<sup>&</sup>lt;sup>3</sup> J. Mocak, A. M. Bond, S. Mitchell and G. Scollary, Pure Appl. Chem., 1997, 69, 297.



Fig. S7 Ultraviolet-visible (UV-vis) absorption a) and fluorescence b) spectra of ZR1 (10<sup>-5</sup> M) in methanol and methanol-water mixtures.  $\lambda_{ex} = 500$  nm, slit = 10 nm, 10 nm.



**Fig. S98** a) UV-vis titration spectra of **ZR1** (10<sup>-5</sup> M) in the presence of different concentrations of methanol in Red Star Erguotou; inset: the ratio ( $A_{568 \text{ nm}}/A_{494 \text{ nm}}$ ) of absorbances as a function of methanol concentration; linear regression equation:  $A_{568}/A_{494} = 0.25659 + 0.01902$  [MeOH] (v/v), R = 0.998; b) Fluorescence titration spectra (10<sup>-5</sup> M) of **ZR1** in the presence of different concentrations of methanol in Red Star Erguotou; inset: the ratio ( $I_{564}/I_{606}$ ) of fluorescence intensities as a function of methanol contention; linear regression equation:  $I_{564}/I_{606} = 1.84661 - 0.03847$  [MeOH] (v/v), R = 0.999.  $\lambda_{ex} = 500$  nm, slit = 10 nm, 10 nm.



**Fig. S9** a) UV-vis spectra of **ZR1** (10<sup>-5</sup> M) in mimic methanol-containing gasolines. The components of the mimic methanol-containing gasolines are petroleum ether (50%) and alcohols (50%), and alcohols were ethanol, and ethanol containing 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% of methanol. Inset: the ratio ( $A_{568 \text{ nm}}/A_{494 \text{ nm}}$ ) of absorbance as a function of methanol content in alcohols; linear regression equation:  $A_{568}/A_{494} = 0.17265 + 0.01626$  [MeOH] (v/v), R = 0.9958; b) Fluorescence spectra (10<sup>-5</sup> M) of **ZR1** in mimic methanol-containing gasolines; inset: the ratio ( $I_{564}/I_{601}$ ) of fluorescence intensities as a function of methanol contention, R<sup>2</sup> = 0.99801.  $\lambda_{ex} = 500 \text{ nm}$ , slit = 10 nm, 10 nm.



Figure S10. <sup>1</sup>H NMR of ZR (400 MHz, CDCl<sub>3</sub>).



Figure S11. <sup>13</sup>C NMR of ZR (100 MHz, CDCl<sub>3</sub>).



Figure S12. HRMS (LC/MS) spectra of ZR1. The peak at m/z = 576.2402 was assigned to the mass of [ZR1 + H<sup>+</sup>].



Figure S13. <sup>1</sup>H NMR of ZR1 (400 MHz, CDCl<sub>3</sub>).



**Figure S14.** <sup>13</sup>C NMR of **ZR1** (100 MHz, DMF-*d*7).

## Table S3 Crystal data and structure refinement for ZR1.

Identification code	ZR1
Empirical formula	$C_{39}H_{38}N_2O_7$
Formula weight	648.74
Temperature/K	293
Crystal system	triclinic
Space group	P1
a/Å	7.0350(17)
b/Å	8.4308(18)
c/Å	15.210(4)
α/°	98.594(19)
β/°	99.03(2)
$\gamma/^{\circ}$	105.311(20)
Volume/Å <sup>3</sup>	841.9(4)
Ζ	1
$\rho_{calc}g/cm^3$	1.276
$\mu/mm^{-1}$	0.088
F(000)	342.0
Crystal size/mm <sup>3</sup>	$0.11\times0.05\times0.05$

Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ )				
Theta range for data collection 5.114 to 54.964					
Index ranges	$-9 \le h \le 9, -7 \le k \le 10, -16 \le i \le 19$				
Reflections collected	4951				
Independent reflections	4429 [ $R_{int} = 0.0335$ , $R_{sigma} = 0.1089$ ]				
Data/restraints/parameters	4429/5/441				
Goodness-of-fit on F <sup>2</sup>	0.968				
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0852, wR_2 = 0.2309$				
Final R indexes [all data]	$R_1 = 0.1785, wR_2 = 0.3390$				
Largest diff. peak/hole / e Å <sup>-3</sup>	0.41/-0.27				
Flack parameter	4.9(10)				

## Table S4 Bond Lengths for ZR1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
COAA	N2	1.475(18)	C9	C18	1.454(13)
C1	C2	1.373(16)	C10	C11	1.442(14)
C1	C22	1.438(14)	C11	C12	1.402(15)
N1	C26	1.412(12)	C11	C16	1.432(15)
N1	C29	1.469(16)	C12	C13	1.420(18)
N1	C33	1.499(18)	C13	C14	1.407(19)
01	C7BA	1.276(16)	C14	C15	1.345(17)
C2	C3	1.371(15)	C15	C16	1.429(15)
N2	C7BA	1.307(14)	C16	C17	1.463(15)
N2	C9BA	1.436(14)	C17	C18	1.418(14)
02	C17	1.348(12)	C18	C19	1.444(14)
C3	C4	1.415(15)	C19	C20	1.475(14)
03	C19	1.276(11)	C20	C21	1.388(13)
C4	C5	1.410(15)	C21	C22	1.437(14)
04	C21	1.353(10)	C23	C24	1.400(13)
C5	C6	1.468(14)	C23	C28	1.408(14)
C5	C22	1.387(14)	C24	C25	1.401(12)

C10	1.329(12)	C25	C26	1.412(13)
C7	1.395(14)	C26	C27	1.400(14)
C23	1.505(13)	C27	C28	1.365(13)
C8	1.259(11)	C29	C30	1.48(2)
C8	1.495(15)	C30	C31	1.46(2)
C20	1.431(13)	C31	C32	1.33(3)
C24	1.379(11)	C33	C34	1.52(2)
С9	1.468(14)	C34	C35	1.62(3)
C10	1.407(14)	C35	C36	1.33(3)
	C10 C7 C23 C8 C8 C20 C24 C9 C10	C101.329(12)C71.395(14)C231.505(13)C81.259(11)C81.495(15)C201.431(13)C241.379(11)C91.468(14)C101.407(14)	C101.329(12)C25C71.395(14)C26C231.505(13)C27C81.259(11)C29C81.495(15)C30C201.431(13)C31C241.379(11)C33C91.468(14)C34C101.407(14)C35	C101.329(12)C25C26C71.395(14)C26C27C231.505(13)C27C28C81.259(11)C29C30C81.495(15)C30C31C201.431(13)C31C32C241.379(11)C33C34C91.468(14)C34C35C101.407(14)C35C36

### Table S5 Bond Angles for ZR1.

Aton	1 Aton	n Atom	Angle/°	Aton	1 Aton	n Atom	Angle/°
C2	C1	C22	118.9(10)	C15	C16	C17	122.0(10)
C26	N1	C29	123.9(10)	02	C17	C16	117.2(9)
C26	N1	C33	119.7(10)	02	C17	C18	122.6(9)
C29	N1	C33	116.4(10)	C18	C17	C16	120.2(9)
C3	C2	C1	121.6(10)	C17	C18	C9	119.4(9)
C7BA	AN2	COAA	119.5(10)	C17	C18	C19	119.5(9)
C7BA	AN2	C9BA	121.9(11)	C19	C18	C9	121.1(8)
C9BA	AN2	COAA	117.8(9)	03	C19	C18	120.5(9)
C2	C3	C4	119.6(11)	03	C19	C20	120.3(9)
C5	C4	C3	120.8(10)	C18	C19	C20	119.1(8)
C4	C5	C6	121.3(9)	C7	C20	C19	122.2(8)
C22	C5	C4	118.2(9)	C21	C20	C7	120.0(9)
C22	C5	C6	120.6(9)	C21	C20	C19	117.9(9)
C5	C6	C23	117.2(9)	04	C21	C20	123.9(9)
C7	C6	C5	117.8(9)	04	C21	C22	116.0(9)
C7	C6	C23	124.9(9)	C20	C21	C22	120.1(9)
C6	C7	C8	120.7(9)	C5	C22	C1	120.9(10)
C6	C7	C20	121.5(9)	C5	C22	C21	120.1(9)
C20	C7	C8	117.8(8)	C21	C22	C1	119.1(10)
01	C7BA	AN2	123.7(12)	C24	C23	C6	121.8(9)
06	C8	C7	122.1(9)	C24	C23	C28	115.5(8)
06	C8	C9	117.2(9)	C28	C23	C6	122.6(9)
C9	C8	C7	120.7(9)	07	C24	C23	118.7(7)
C10	C9	C8	120.2(9)	07	C24	C25	119.4(8)
C10	C9	C18	120.7(8)	C23	C24	C25	121.9(9)
C18	C9	C8	119.1(9)	C24	C25	C26	120.1(8)
05	C10	C9	122.4(9)	C25	C26	N1	118.2(8)

05	C10	C11	117.2(9)	C27	C26	N1	123.2(9)
C9	C10	C11	120.4(10)	C27	C26	C25	118.6(8)
C12	C11	C10	120.4(11)	C28	C27	C26	119.4(9)
C12	C11	C16	119.7(10)	C27	C28	C23	124.4(9)
C16	C11	C10	119.9(10)	N1	C29	C30	116.1(13)
C11	C12	C13	119.0(13)	C31	C30	C29	116.3(19)
C14	C13	C12	120.8(12)	C32	C31	C30	120(2)
C15	C14	C13	120.1(11)	N1	C33	C34	114.2(14)
C14	C15	C16	121.6(11)	C33	C34	C35	113.3(17)
C11	C16	C17	119.4(9)	C36	C35	C34	114(2)
C15	C16	C11	118.7(10)				