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Supporting Information

Broad-Spectrum Chemiluminescence Covering 400-1400 nm Spectral Region and its Use as White-Near Infrared Light Source for Imaging

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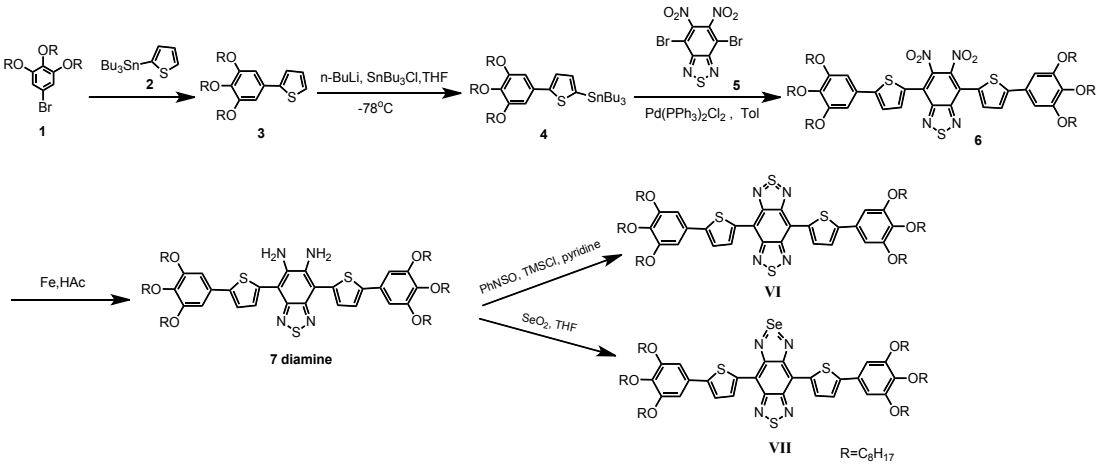
Characterization of polymeric fluorophore I

GPC: The number-average molecular weight (M_n) of the polymer (I) is 52.7 kDa, and the polydispersity index (PDI) is 2.4. The value of n is approximately 135.

Synthesis and characterizations of VI and VII

5-Bromo-1,2,3-trioctyloxybenzene (**1**)[1] and 4,7-dibromo-5,6-dinitro-2,1,3-benzothiadiazole (**5**)[2] were prepared according to literature methods. Compounds **VI** and **VII** were synthesized according to Scheme S1.



Scheme S1. Synthetic routes to compounds **VI** and **VII**

2-(3,4,5-Tris(octyloxy)phenyl)thiophene (3). Compound **1** (19.60 g, 36.18 mmol), compound **2** (19.61 g, 43.42 mmol) and $Pd(PPh_3)_2Cl_2$ (50.5 mg, 0.072 mmol) were added into dry toluene (250 mL). The mixture was refluxed under an argon atmosphere for 16 h. After cooling to room temperature, the reaction mixture was diluted with aqueous KF solution and then extracted with dichloromethane. The organic layer was collected and washed with brine and then dried over anhydrous sodium sulfate. The product was obtained as light yellow liquid (17.53 g, 88.8%) after column chromatography (silica gel, ethyl acetate/petroleum ether = 1/50, V/V). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.24 (d, 1H), 7.21 (d, 1H), 7.06-7.03 (m, 1H), 6.78 (s, 2H), 4.04-3.93 (m, 6H), 1.85-71.72 (m, 6H), 1.50-1.29 (m, 30H), 0.90 (t, 9H).

Tributyl(5-(3,4,5-tris(octyloxy)phenyl)thiophen-2-yl)stannane (4). 2-(3,4,5-Tris(octyloxy)phenyl)thiophene (**3**) (2.72 g, 5.00 mmol) was dissolved in dry THF and maintained at -80 °C (dry ice-acetone bath). *n*-BuLi (1.72 mL, 5.00 mmol, 2.9 mol/L) was added to the solution above slowly and stirred for two hours. Then Bu_3SnCl (1.63 mL, 6.00 mmol) was introduced into the reaction and the stirring continued for 3 hours at -80 °C. The reaction continued overnight at room temperature. The reaction solution was washed with water, extracted with dichloromethane and dried over anhydrous sodium sulfate. After filtration and evaporation, the crude product was used for the next reaction without further purification.

5,6-Dinitro-4,7-bis(5-(3,4,5-tris(octyloxy)phenyl)thiophen-2 yl)benzo[*c*][1,2,5]thiadiazole (6). A solution of compound **5** (2.71 g, 7.05 mmol), compound **4** (22.98 g, 16.92 mmol) and $Pd(PPh_3)_2Cl_2$ (15 mg, 0.021 mmol) in dry toluene were refluxed in an argon atmosphere for 48 h. After cooling to room temperature, the reaction solution was washed by aqueous KF solution and then extracted with dichloromethane. The organic layer was collected and washed with brine and then dried over anhydrous sodium sulfate. The product was obtained as deep purple solid (8.407 g, 90.9%) after column chromatography (silica gel, dichloromethane /petroleum ether = 1/3, V/V). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.49 (d, 2H), 7.31 (d, 2H), 6.84 (s, 4H), 4.06-3.94 (m, 12H), 1.87-1.73 (m, 12H), 1.50-1.28 (m, 60H), 0.91-0.87 (m, 18H).

4,7-Bis(5-(3,4,5-tris(octyloxy)phenyl)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole-5,6-diamine (7). Compound **6** (3.96 g, 3.02 mmol) and iron powder (2.03 g, 36.20 mmol) were added to 100 mL of THF, followed by addition of acetic acid (200 mL). The mixture was heated to 80 ^{o} C for 64 h. After cooling, the mixture was poured into water and extracted with toluene. The organic layer was washed with saturated $NaHCO_3$ solution for three times and dried over anhydrous sodium sulfate. After filtration and evaporation, the crude product was purified by column chromatography (silica gel, dichloromethane as eluent), which gave compound **7** as a brown solid (1.99 g, 52.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.34 (s, 4H), 6.85 (s, 4H), 4.06-3.98 (m, 12H), 1.87-1.73 (m, 12H), 1.51-1.30 (m, 60H), 0.91-0.87 (m, 18H).

Compound VI. A solution of compound **7** (0.25 g, 0.2 mmol), N-sulfinylaniline (55.7 mg, 0.4 mmol) and chlorotrimethylsilane (43.5 mg, 0.4 mmol) in dry pyridine (20 mL) was stirred at 80 ^{o}C for 16 h under an argon atmosphere. After cooling to room temperature, pyridine was removed under vacuum. The residue was purified by column chromatography (silica gel, dichloromethane/petroleum ether=1/2, V/V) to give compound **VI** as a blue solid (0.15 g, 58.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.94 (s, 2H), 7.41 (s, 2H), 6.96 (s, 4H), 4.02-4.10 (m, 12H), 1.79-1.87 (m, 12H), 1.31-1.53 (m, 60H), 0.90 (t, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.50, 150.86, 149.39, 138.86, 137.01, 133.67, 129.33, 123.82, 112.84, 104.78, 73.64, 69.37, 31.96, 31.90, 30.45, 29.64, 29.57, 29.50, 29.44, 29.38, 26.24, 26.20, 22.72, 14.13. MALDI-TOF-MS: m/z 1278.7.

Compound VII. A solution of compound **7** (0.256 g, 0.2 mmol) and selenium dioxide (56 mg, 0.5 mmol) in dry THF (25 mL) was stirred at 66 ^{o}C for 10 h under an argon atmosphere. THF was removed under vacuum at 30 ^{o}C. The residue was purified by column chromatography (neutral alumina, dichloromethane/petroleum ether=1/2, V/V) to give **VII** as a black brown solid (0.25 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.95 (s, 2H), 7.40 (s, 2H), 6.96 (s, 4H), 4.01-4.10 (m, 12H), 1.75-1.88 (m, 12H), 1.26-1.57 (m, 60H), 0.88-0.92 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.16, 152.39, 149.63, 148.65, 137.78, 137.06, 133.30, 128.30, 122.53, 111.51, 103.63,

72.64, 68.32, 30.95, 30.90, 29.47, 28.64, 28.59, 28.52, 28.43, 28.38, 25.26, 25.21, 21.71, 13.11. MALDI-TOF-MS: m/z 1326.7.

Fluorescence quantum yields

The common method of calculating the quantum yield of a fluorophore is by comparison with a standard of known quantum yield. The used standards and the relative information in this work are listed in Table S1.

Table S1 Fluorescence Quantum Yield Standards

Quantum Yield [Q.Y.] Standards	Q.Y.[%]	Conditions for Measurement	Excitation [nm]	Ref.
Quinine Sulfate	55	0.5 M H_2SO_4, 25 °C	350	3
Fluorescein	95	0.1 M NaOH, 22 °C	496	3
IR-125	13	DMSO, 25 °C	700	4

Emission quantum yields in solution were measured by the method in reference.[5] Diluted solutions of different dye concentrations (A < 0.1) were prepared and the absorbance (A) and the integrated fluorescence intensity (D) at each concentration were recorded at given excitation wavelengths the same as the standards. Then a graph of D versus A was plotted to determine the gradient (G). Equation of quantum yields (Φ) was shown below.

$$\Phi_s = \Phi_r \left(\frac{G_s}{G_r}\right)\left(\frac{I(\lambda_r)}{I(\lambda_s)}\right)\left(\frac{n_s}{n_r}\right)^2$$

The subscripts *r* and *s* refer to the reference dyes and the samples, respectively. *n* is the refractive index of the solvent. *I(λ)* is the relative intensity of the light at excitation wavelength.

Process of CL reaction

Preparations before CL reaction: Three solutions were needed. Solutions of fluorophores with a concentration of 1 ×10^{-5} M and oxalyl chloride with a concentration of 1.149 M were prepared in dried chloroform, respectively. The solution of hydrogen peroxide (30% in H_2O) were diluted to a concentration of 2.48 M in dried THF.

Procedure for single-fluorophore chemiluminescence: 50 μL of solution of

hydrogen peroxide (2.48 M) was added into solutions of fluorophores (1×10^{-5} M, 3 mL) by pipette and mixed intensively. Then the mixture was transferred into a quartz cuvette, put into a UV-vis fluorimeter or PTI fluorescence system and then the intensity at fixed wavelength can be recorded as a baseline with the time going. It is notable that the light outside and excitation beam from the fluorimeter have been turned off to avoid the interference from the external light. 100 uL of solution of oxalyl chloride (1.149 M) was manually added into the mixture above through a microsyringe rapidly and the changes of intensity can be observed almost simultaneously and recorded by the fluorimeter: the CL intensity markedly increased once the CL reaction began and then decreased after very short time. The final volume of the working solution was 3.15 mL and the concentrations of the reactants can be calculated as fluorophores (9.52×10^{-6} M), hydrogen peroxide (3.93×10^{-2} M) and oxalyl chloride (3.65×10^{-2} M).

For multi-fluorophore chemiluminescence, the similar operations have been done as described above except for adjusting proper proportions of each of fluorophores when blending together.

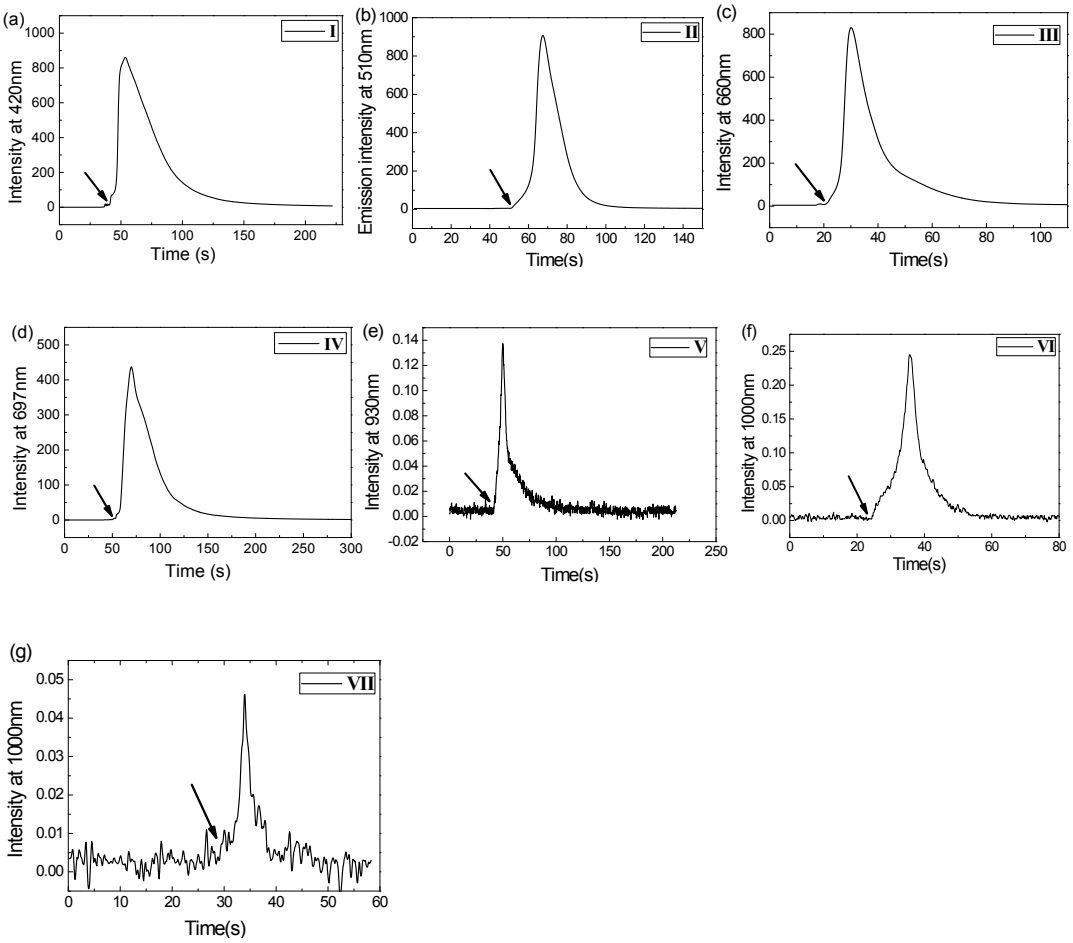


Fig. S1 CL flash emission monitored at the fixed emission wavelength from the reaction of oxalyl chloride, hydrogen peroxide and fluorophores **I** to **VII**. Exact time points for the injection of oxalyl chloride are marked with black arrows for each fluorophore.

Table S2 Durations of the CL Light and HOMO Values of Seven Fluorophores

fluorophore	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**
t $_{1/2}$ (s) [a]	28.9	12.4	9.9	28.6	5.9	5	2.1
HOMO (eV) [b]	-5.57	-5.41	-5.32	-5.52	-5.18	-5.09	-5.01

[a] Full width at half-maxima.

[b] Calculated from the formula, $E_{(HOMO)}$=—(E_{ox}+ 4.43) (eV)

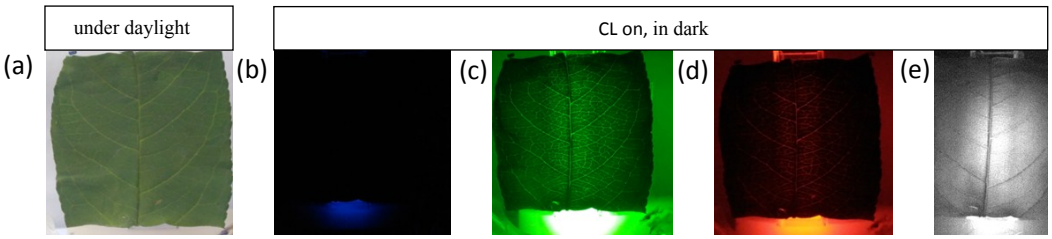
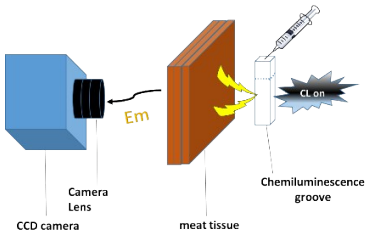


Fig. S2 CL imaging of single fluorophore for leaf. Photographs in (a-d) were taken by a colour camera: Daylight (a), CL light of **I** (b), CL light of **II** (c) and CL light of **III** (d). Photograph in (e) was taken by a NIR camera under CL light from **V**, **VI** or **VII**.

(a)



(b)

Tissue thickness	no tissue	3.8mm	7.3mm	9.6mm	1.55cm	1.87cm
Images						

Fig. S3 Penetration of fresh meat tissues using the white- NIR CL source in present work: experimental set-up (a) and photographs taken by a NIR camera after the CL light passing through several thicknesses of tissues (b). Concentrations: Hydrogen peroxide (1.96×10^{-1} M), oxalyl chloride (1.46×10^{-2} M), the concentrations of fluorophores **I**-**VII** were about ten times as those for the white-NIR CL imaging of the leaf and mouse.

References

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