Electronic Supplementary Information

Adjustment of Solid Fluorescence of Chalcone Derivatives through Controlling Steric Hindrance

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Experimental

Materials

Allyl bromide, 2-hydroxy-1-naphthaldehyde and 4-vinylbenzyl chloride were purchased from TCI(Shanghai). Other chemicals and solvents were used directly without further purification.

Characterization

Using CDCl₃ as solvents and tetramethylsilane (TMS) as the internal standard, ¹H NMR and ¹³C NMR spectra were measured on a Bruker Advance 400 and 600 NMR spectrometer at ambient temperature. UV-vis absorption spectra were obtained from a Shimidazu UV-3600 spectrophotometer. High resolution mass spectra (HRMS) were obtained from a MicroMass TOF-MS spectrometer (EI).

Fluorescence microscope measurement. Fluorescence image was obtained using a Nikon Ti-U Inverted Microscope System equipped with a Nikon C-SHG 1 mercury lamp. The exposure time to acquire a bright photo on a fluorescence microscope is 200 ms, with four attenuators (1/4, 1/8, 1/16, and 1/32).

The fluorescent quantum yields in dilute solutions were determined using quinine bisulfate $(\varphi = 54.6\% \text{ in } 0.1 \text{ N H}_2\text{SO}_4)$ as a standard using the equation:

$$\phi_s = \frac{F_s}{F_r} \frac{n_s^2}{n_r^2} \frac{A_r}{A_s} \phi_r \tag{1}$$

In this equation, subscripts s and r represent the sample and reference, respectively. F is the integral area of the fluorescence spectra, n is the refractive index of the solution, A is the absorbance, is the fluorescence quantum yield.

Photoluminescence spectra (PL) and fluorescence quantum yield for solid state were collected on an Edinburgh Instruments FLS 980 system spectrofluorimeter equipped with Xe-900 and integrating sphere.

Synthesis

The synthetic procedure for the preparation of compounds ANPEO and VBNPEO is displayed in

Scheme 1. Compounds ANPEO and VBNPEO were characterized by ¹H and ¹³C NMR spectroscopy, mass spectrometry and single crystal analysis.



Scheme S1. Synthesis routine of compound ANPEO and VBNPEO.

Synthesis of 2-(allyloxy)-1-naphthaldehyde (AN)

A mixture of 2-hydroxy-1-naphthaldehyde (10 mmol, 1.72 g), allyl bromide (12 mmol. 1.44 g), and potassium carbonate (10 mmol, 1.38 g) were stirred in acetone (50 mL) under N₂ atmosphere. The result mixture solution was refluxed for 24 hr. After cooling to room temperature, the result mixture solution was poured into a water-ice bath (300 mL). The crude powder was obtained and further purified by recrystallization from ethanol-water. Yield, 72%, 7.2 mmol, 1.53 g.

¹H NMR (400 MHz, CDCl₃) δ 11.06 (s, 1H), 9.27 (s, 1H), 8.03 (s, 1H), 7.76 (s, 1H), 7.61 (s, 1H), 7.42 (s, 1H), 7.27 (s, 1H), 6.09 (s, 1H), 5.47 (d, *J* = 11.2 Hz, 1H), 5.35 (s, 1H), 4.79 (s, 2H).

Synthesis of 2-((4-vinylbenzyl)oxy)-1-naphthaldehyde (VBN)

2-((4-Vinylbenzyl)oxy)-1-naphthaldehyde was obtained in 65% yield (6.5 mmol, 1.87 g) from the reaction between 2-hydroxy-1-naphthaldehyde (10 mmol, 1.72 g), 4-vinylbenzyl chloride (12 mmol. 1.82 g), and potassium carbonate (10 mmol, 1.38 g) by following the general procedure described for 2-(allyloxy)-1-naphthaldehyde.

¹H NMR (400 MHz, CDCl₃) δ 10.98 (s, 1H), 9.28 (d, *J* = 8.7 Hz, 1H), 8.03 (d, *J* = 9.1 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.50 – 7.37 (m, 5H), 7.33 (d, *J* = 9.1 Hz, 1H), 6.73 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.78 (d, *J* = 17.6 Hz, 1H), 5.33 (s, 2H), 5.29 (d, *J* = 10.8 Hz, 1H). Synthesis of 3-(2-(allyloxy)naphthalen-1-yl)-1-phenylprop-2-en-1-one (ANPEO) The solution of acetic acid (60 mL) containing 2-(allyloxy)-1-naphthaldehyde (1.06 g, 5 mmol) was added into the solution of sulfuric acid (2 mL) including acetophenone (0.66 g, 5.5 mmol). The result mixture solution was stirred at room temperature for 24 hr, and was poured into a ice-water bath (500 mL). The pH of the solution was adjusted to neutral with 0.1 mol L⁻¹NaOH. The crude powder was collected by filtration. The pure green powder (0.86 g, 2.75 mmol, yield: 55%) was recrystallized twice from the mixture solution of ethanol and water.

¹H NMR (400 MHz, CDCl₃) δ 8.52 (d, *J* = 15.7 Hz, 1H), 8.27 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 5.8 Hz, 2H), 7.97 (d, *J* = 15.6 Hz, 1H), 7.84 (dd, *J* = 21.7, 7.9 Hz, 2H), 7.63 – 7.47 (m, 4H), 7.41 (s, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 6.24 – 6.07 (m, 1H), 5.49 (d, *J* = 17.2 Hz, 1H), 5.35 (d, *J* = 10.2 Hz, 1H), 4.80 (s, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 191.18, 156.11, 138.54, 137.67, 133.12, 132.97, 132.58, 131.70,
129.14, 128.58, 128.50, 127.48, 127.40, 124.11, 123.46, 118.29, 117.85, 114.17, 70.10.
MS, formula, C₂₂H₁₉O₂; Calc. mass, 315.1385; found, 315.1356.

Synthesis of 1-phenyl-3-(2-((4-vinylbenzyl)oxy)naphthalen-1-yl)prop-2-en-1-one (VBNPEO)

1-Phenyl-3-(2-((4-vinylbenzyl)oxy)naphthalen-1-yl)prop-2-en-1-one was obtained in 50% yield from the reaction between 2-((4-vinylbenzyl)oxy)-1-naphthaldehyde and acetophenone by following the general procedure described for 3-(2-(allyloxy)naphthalen-1-yl)-1-phenylprop-2-en-1-one.

¹H NMR (400 MHz, CDCl₃) δ 8.61 (s, 1H), 8.33 (s, 1H), 7.86 (dd, *J* = 66.7, 27.2 Hz, 6H), 7.42 (dd, *J* = 28.3, 21.0 Hz, 9H), 6.77 (s, 1H), 5.81 (d, *J* = 16.5 Hz, 1H), 5.30 (s, 3H).
¹³C NMR (151 MHz, CDCl₃) δ 190.93, 156.63, 138.40, 137.75, 136.90, 136.32, 135.74, 133.47, 132.44, 131.97, 129.13, 128.64, 128.59, 128.49, 128.43, 127.58, 126.64, 124.15, 123.29, 117.23, 114.55, 113.83, 71.22.

MS, formula, C₂₈H₂₂NaO₂; Calc. mass, 413.1517; found, 413.1524.



Figure S2. ¹³C NMR spectrum of ANPEO in CDCl₃.



Figure S4. ¹H NMR spectrum of VBNPEO in CDCl₃.



Figure S5¹³C NMR spectrum of VBNPEO in CDCl₃.



Figure S7. UV-vis absorption spectra of VBNPEO in different solvents.



Figure S8. Emission spectra of compound ANPEO in different solvents ($\lambda_{ex} = 373$ nm).



Figure S9. Emission spectra of compound VBNPEO in different solvents ($\lambda_{ex} = 373$ nm).



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