# Synthesis of Tripodal Naphthylacetamide Derivatives

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A tripodal naphthylacetamide derivative (I and II) used as a new enhancement fluorescence chemical sensor for detection of transition metal ions has been synthesized in this work. Two new derivatives were prepared in good yields according to the proposed method. The products were characterized by elemental analysis, <sup>1</sup>H NMR spectra, and mass spectrometry (MS).

Keywords: Synthesis; Tripodal naphthylacetamide; Fluorescence; Transition metal ion.

In past years, the study of fluorescence chemical sensors in which a fluorescence emission group and a foreign object receiving group compose a fluorescence signal system for detection of foreign objects, has been highly regarded by chemists.<sup>1,2</sup> Fluorescence intensity receiving objects of some d orbit full transition metal ions were reported by Fabbizzi<sup>3</sup> and Czarnik.<sup>4</sup> As we know, transition metal ions play an important role in biochemistry and environmental chemistry, and transition metal ions have stronger extinguishments of fluorescence intensity.<sup>5,6</sup> So people have attempted to find easier and better methods for synthesizing a fluorescence chemical sensor of enhancement fluorescence intensity after it combines with transition metal ions. Recently, fluorescence chemical sensors (substance) were reported by Ghosh<sup>7</sup> and Samanta,<sup>8</sup> respectively. In this paper, a tripodal naphthylacetamide derivative (I and II) used as a new enhancement fluorescence chemical sensor for detection of transition metal ions has been synthesized. The synthesis of compounds is summarized as follows.

The overall yield of the products is 69.6% (I) and 69.5% (II), respectively. During the synthesis, only a little solvent was used and no protecting groups were introduced. The compounds were characterized by elemental analysis, <sup>1</sup>H NMR spectra, and mass spectrometry (MS).



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The compound (I and II) shows excellent complexing properties and enhancement fluorescence towards some transition metal ions. For example, the compound clearly enhances fluorescence intensity after introduction of the transition metal ions  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Cr^{3+}$ ,  $Mn^{2+}$ .

### **EXPERIMENTAL**

4-Dimethylaminopyridine (DMAP, Shanghai, China), N,N-dicyclohexanemethanamide (DCA, Shanghai, China), tri(2-aminoethyl)amine (TAEA, Shanghai, China), 1-naphthylacetic acid (Xian, China); all other reagents and solvents used were analytical grade. <sup>1</sup>H NMR data were obtained on a Varian Gemini (300 MHz) instrument. Elemental analyses were performed by a Heraeus CHN Elemental Analyzer. MS spectra were recorded on a Finnigan 4021c Gc-MS mass spectrometry Instrument.

### p-Nitrophenyl-1-naphthylacetate

1-Naphthylacetic acid (1.86 g, 10 mmol), p-nitrophenol (1.39 g, 10 mmol), and DMAP (70 mg) were dissolved in 40 mL dry dichloramethane (CH<sub>2</sub>Cl<sub>2</sub>) and the mixture was cooled to 0 °C. Then DCA (2.11 g, 10.2 mmol) was added to the mixture. The reaction solution was whisked for 1 h; the mixture was heated to room temperature. The reaction solution was whisked for 4 h again. The mixture was filtered; so-

lution was separated by silica gel column, washed with dichloramethane (CH<sub>2</sub>Cl<sub>2</sub>) and finally dried in vacuum over anhydrous CaCl<sub>2</sub>. m.p.: 76-78 °C. yield: 87%. Elemental analysis calculated for C<sub>18</sub>H<sub>13</sub>NO<sub>4</sub> (Found): C 70.36 (69.99); H 4.23 (4.20); N 4.56 (4.60); <sup>1</sup>H NMR (300 MHz, DMSO):  $\delta$ : 7.2-8.4 (m, 11H, ArH), 4.5 (s, 2H, ArCH<sub>2</sub>).

#### Tri(1-naphthylacetamideethyl)amine (I)

TAEA (0.195 mL, 1.33 mmol), p-nitrophenyl-1-naphthylacetate (1.228 g, 4 mmol) were dissolved in 20 mL dry dichloramethane (CH<sub>2</sub>Cl<sub>2</sub>), and then added to 1 mL N (CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>. The solution mixture was whisked for 2 h; the solution changes to yellow. The solution was separated by silica gel column, washed with dichloramethane (CH<sub>2</sub>Cl<sub>2</sub>) and finally dried in vacuum over anhydrous CaCl<sub>2</sub>. m.p.: 221 °C. yield: 80%. Elemental analysis calculated for C<sub>42</sub>H<sub>42</sub>N<sub>4</sub>O<sub>3</sub> (Found): C 77.51 (76.52); H 6.50 (6.46); N 8.61 (8.63); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ : 7.78 (m, 21H, ArH), 6.02 (s, 3H, CONH), 3.95 (s, 6H, ArCH<sub>2</sub>), 2.77 (t, 6H, 3NHCH<sub>2</sub>), 2.16 (t, 6H, 3CH<sub>2</sub>N), *m/z*: 650 (M<sup>+</sup>), 452 (2.5%), 212 (31.92%), 168 (56.62%), 141 (100%), 115 (31.88%).

#### p-Nitrophenyl-5-nitro-1-naphthylacetate

5-Nitro-1-naphthylacetic acid (2.31 g, 10 mmol), pnitrophenol (1.39 g, 10 mmol), and DMAP (80 mg) were dissolved in 40 mL dry dichloramethane (CH<sub>2</sub>Cl<sub>2</sub>), and the mixture was cooled to 0 °C. Then DCA (2.11 g, 10.2 mmol) was added to the mixture. The reaction solution was whisked for 1.5 h; the mixture was heated to room temperature. The reaction solution was whisked for 5 h again. The mixture was filtered; the solution was separated by silica gel column, washed with dichloramethane (CH<sub>2</sub>Cl<sub>2</sub>) and finally dried in a vacuum over anhydrous CaCl<sub>2</sub>. m.p.: 86-87 °C. yield: 88%. Elemental analysis calculated for C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub> (Found): C 61.36 (61.69); H 3.41 (3.60); N 7.96 (8.00); <sup>1</sup>H NMR (300 MHz, DMSO):  $\delta$ : 7.85 (m, 10H, ArH), 4.6 (s, 2H, ArCH<sub>2</sub>).

### Tri(5-nitro-1-naphthylacetamideethyl)amine (II)

TAEA (0.195 mL, 1.33 mmol), p-nitrophenyl-5-nitro-1-naphthylacetate (1.408 g, 4 mmol) were dissolved in 20 mL dry dichloramethane (CH<sub>2</sub>Cl<sub>2</sub>), and then added to 1 mL N (CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>. The solution mixture was whisked for 3 h; the solution changes to yellow. The solution was separated by silica gel column, washed with dichloramethane (CH<sub>2</sub>Cl<sub>2</sub>) and finally dried in a vacuum over anhydrous CaCl<sub>2</sub>. m.p.: 252 °C. yield: 79%. Elemental analysis calculated for C<sub>42</sub>H<sub>39</sub>N<sub>7</sub>O<sub>9</sub> (Found): C 64.18 (64.52); H 4.97 (5.03); N 12.48 (12.60); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ : 7.80 (m, 18H, ArH), 6.02 (s, 3H, CONH), 3.95 (s, 6H, ArCH<sub>2</sub>), 2.80 (t, 6H, 3NHCH<sub>2</sub>), 2.18 (t, 6H, 3CH<sub>2</sub>N), *m/z*: 785 (M<sup>+</sup>), 542 (3.2%), 257 (33.02%), 203 (55.02%), 186 (100%), 160 (34.86%).

# Enhanced fluorescence of the Tri(1-naphthylacetamideethyl)amine (I)

The fluorescence spectra of compound (I) are shown Fig. 1 in acetonitrile. Excitation wavelength is between 325



Fig. 1. Fluorescence spectra of compounds in acetonitrile. (a) compound (I):  $5 \times 10^{-5}$  mol/L; (b) compound (I) +  $5 \times 10^{-5}$  mol/L Cu<sup>2+</sup>; (c) naphthalene 1.67 × 10<sup>-5</sup> mol/L.

nm and 350 nm; the wavelength of profile and value are quite similar to naphthalene. The fluorescence intensity of compound (I) is less than the fluorescence intensity of naphthalene at the same concentration of naphthyl. The  $Cu^{2+}$  can enhance fluorescence intensity of compound (I).

In this work, the effect of various transition metal ions to fluorescence intensity of the compounds (I, II) were studied. Fig. 2 shows fluorescence intensity of the compound (I) at 340 nm and Fig. 3 shows fluorescence intensity of the com-



Fig. 2. Fluorescence intensity of compound (I) at 340 nm as a function of concentration of various transition metal ions. 1-Zn<sup>2+</sup>; 2-Cu<sup>2+</sup>; 3-Ni<sup>2+</sup>; 4-Co<sup>2+</sup>; 5-Fe<sup>2+</sup>; 6-Cr<sup>3+</sup>; 7-Mn<sup>2+</sup>.



Fig. 3. Fluorescence intensity of compound (II) at 345 nm as a function of concentration of various transition metal ions. 1-Co<sup>2+</sup>; 2-Zn<sup>2+</sup>; 3-Mn<sup>2+</sup>; 4-Cu<sup>2+</sup>; 5-Ni<sup>2+</sup>; 6-Fe<sup>2+</sup>; 7-Cr<sup>3+</sup>.

pound (II) at 345 nm as a function of concentration of various transition metal ions. From Fig. 2 and Fig. 3, we can know various transition metal ions as the effect of fluorescence intensity of the compound (I) and compound (II) are not the same, but they all can enhance fluorescence intensity of compound (I) and compound (II).

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