

# Synthesis and photophysical properties of 1, 4-disubstituted naphthyloxymethyl-N-alkyl naphthimido-1,2,3-triazole

J RAMCHANDER, N RAMESHWAR, T SHESHASHENA REDDY, GAJULA RAJU and A RAM REDDY\*

Department of Chemistry, Osmania University, Hyderabad 500 007, India  
e-mail: a\_ramreddy@yahoo.com

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**Abstract.** Regioselective synthesis of a series of 1,4-disubstituted of naphthoxymethyl-N-alkyl naphthalimide-1,2,3-triazoles employing click reaction is presented. Highly selective and efficient copper(I)-catalysed 1,3-dipolar cyclo addition between 1-naphthylpropargylic ether and azido alkyl naphthalimides yielded the title compounds in 74% to 94%. The structure of all the new 1,2,3-triazoles was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and Mass. The electronic absorption and emission studies revealed that the light absorbing and emitting chromophore is the naphthoxy moiety. There is no extensive delocalization of aromatic  $\pi$ -electrons in the active chromophore which exhibited lower quantum yields and lower Stokes shifts.

**Keywords.** Naphthylpropargylic ether; azidonaphthalimides; 1,3-dipolar cycloaddition; regioselective.

## 1. Introduction

With increasing demand in developing fluorescent chemosensors for the detection of biological and environmental analytes, modular approaches have offered the possibility for rapidly constructing sensor molecular libraries. Among them, Cu(I)-catalysed azidealkyne cyclo addition (CuAAC)<sup>1,2</sup> represents one of the most efficient approaches for chemical transformation to create new fluorescent molecules with desired spectral properties.<sup>3–13</sup> The triazoles and substituted triazoles on conjugation with oxadiazoles were developed into organic light emitting diodes by Lee *et al.*<sup>14</sup> who found that triazoles are efficient electron transporting molecules. Ruan and co-workers<sup>15</sup> have investigated the chemo-sensing ability of 1,4 and 1,5 mono- and bi-substituted 1,2,3-triazoles and found that when attached aromatic ring leads to extensive delocalization of  $\pi$ -electrons reducing the energy gap of  $\pi$ - $\pi^*$  transition. Further, they proved that these triazoles are potential ligands because of their N3, N3 and C5 are able to coordinate to metal centres. The ligand character of triazoles was further proved by Jia *et al.* who exploited the naphthol–triazole system for Al<sup>3+</sup> detection, based on chelation-enhanced fluorescence technique.<sup>16</sup> Czirok and co-workers<sup>17</sup> investigated the aminophthimide-based three-armed fluorescent triazole receptors fluorescing of the nucleoside

polyphosphate. Bag, Kundu and Talukdar<sup>18</sup> demonstrated that click triazolenitrogens are binding sites for the selective recognition of metal ions. They have shown that triazolyl units are capable of installation of fluorescence properties into a non-fluorescent precursor and also electronic coupling between a triazole and a fluorophore gives rise to a modulated emission response to the fluorophore, solvatochromism and quantum yield. Triazole derivatives are known to exhibit various pharmacological properties such as anti-microbial,<sup>19</sup> anti-inflammatory,<sup>20</sup> cytotoxic,<sup>21</sup> anti-convulsant,<sup>22</sup> analgesic<sup>23</sup> and anti-viral.<sup>24</sup> Triazoles have also been incorporated in a wide variety of therapeutically interesting drugs including H1/H2 histamine receptor and antimycotic drugs such as fluconazole, itraconazole and voriconazole. On the other hand, heterocycles containing the naphthol nucleus also exhibit various biological activities. For instance, 2-naphthol derivatives have been reported as potential cognition enhancers.<sup>25</sup> 2-Substituted-1-naphthol derivatives were shown to inhibit the activities of cyclooxygenase and 5-lipoxygenase. 1-Naphthol derivatives were found to possess potent anti-amnesic activity. Pharmacological importance and electronic properties of both triazoles and naphthol moiety have encouraged us to synthesize a series of novel 1,4-disubstituted naphthyloxy methyl-N-alkyl naphthimido-1,2,3-triazoles derivatives containing a 1,2,3-triazole. The synthetic route utilized the ‘click reaction’ which is a Cu(I)-catalysed [3+2] cycloaddition popularized by Sharpless as the

\*For correspondence

key transformation to build up the triazole ring.<sup>26</sup> Herein, we report the facile regioselective synthesis of a series of naphthol-based 1,2,3-triazoles employing click reaction and their electronic absorption and emission properties. Electronic absorption and emission studies revealed that the electron transporting ability of 1,4-disubstituted 1,2,3-triazoles did not give a new fluorophore as the conjugation between the two terminal substituents is prevented by the sp<sup>3</sup>-hybridized atoms such as carbon, nitrogen and oxygen.

## 2. Experimental

### 2.1 Materials and apparatus

Spectroscopic grade organic solvents were obtained from Finar Chemicals. Starting and other chemicals and reagents were purchased from Sigma–Aldrich unless otherwise stated and were used without further purification. Thin layer chromatography (TLC) was performed on silica gel 60 F<sub>254</sub> aluminum plates (Merck). The reported melting points were uncorrected and determined in Polmon instrument (model No. MP-96). The IR spectra were recorded on Bruker Infrared model Tensor-27. <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on a Bruker400 MHz Ultrashield spectrometer. The ESI mass spectra were recorded on a VG micro mass 7070-H. UV-vis spectra were recorded on Elico SL 159 UV-VIS spectrophotometer. Steady state fluorescence was investigated on Shimadzu RF-5301PC

spectrofluorophotometer with 5 nm excitation and emission slit widths at 25°C employing 1 cm path length quartz cell. The relative fluorescence quantum yield,  $\Phi$  is evaluated by employing Eq. 1.

$$\Phi_{\text{unk}} = \Phi_{\text{std}} \left( \frac{I_{\text{unk}}}{I_{\text{std}}} \right) \left( \frac{A_{\text{std}}}{A_{\text{unk}}} \right) \left( \frac{n_{\text{unk}}}{n_{\text{std}}} \right)^2, \quad (1)$$

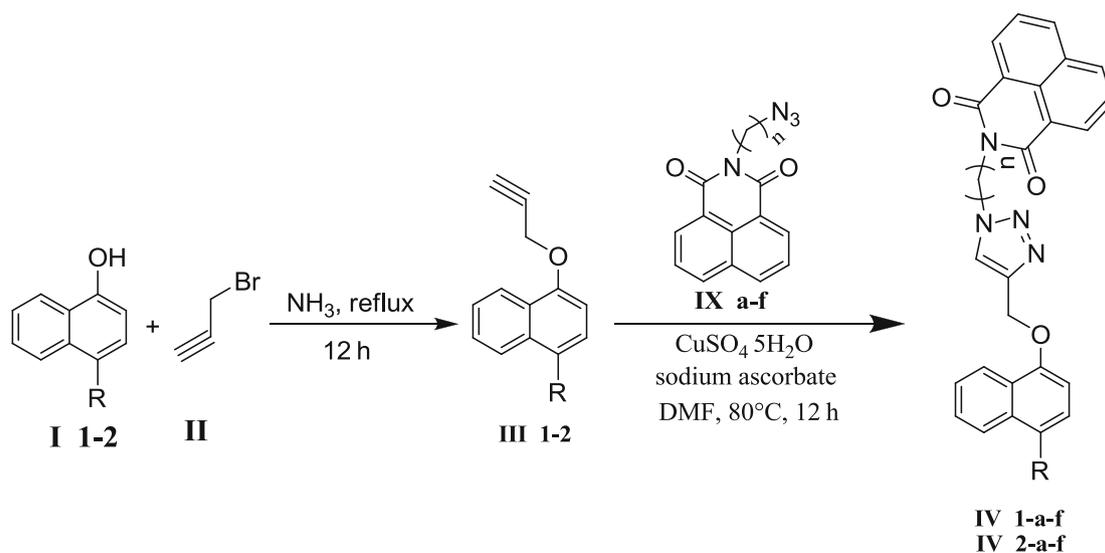
where  $\Phi$ ,  $\Phi_{\text{std}}$ ,  $I_{\text{unk}}$ ,  $I_{\text{std}}$ ,  $A_{\text{std}}$ ,  $A_{\text{unk}}$ ,  $n_{\text{unk}}$  and  $n_{\text{std}}$  are fluorescence quantum yields, integral of the emission intensities, the absorbance at the excitation wavelength and refractive indexes of the corresponding solvents of the unknown samples and the standard, respectively. 9,10-diphenyl anthracene was used as standard in cyclohexane solvent ( $\Phi = 0.9$ ).

### 2.2 General procedure for the synthesis of naphthylpropargylic ethers (III-2)

Naphthylpropargylic ethers were synthesized starting from compound I as shown in scheme 1. Naphthylpropargylic ethers (III) were synthesized according to reported procedure.<sup>27</sup>

### 2.3 General experimental procedure for the synthesis of 1,4-disubstituted naphthoxy methyl-N-alkyl naphthimido-1,2,3-triazoles.(IV1-2 a-f)

Compound III<sub>1-2</sub> (2 mmol) and azides IX<sub>a-f</sub> (2 mmol) were dissolved in 10 mL of DMF. To this mixture, CuSO<sub>4</sub>·5H<sub>2</sub>O (25 mg, 0.1 mmol) and sodium ascorbate



**Scheme 1.** Synthesis of 1,4-disubstituted naphthoxy methyl-N-alkyl naphthimido-1,2,3-triazoles.

(39 mg, 0.2 mmol) aqueous solution were added and stirred at 80°C for 12 h. The reaction mixture was poured into 25 mL of water and was extracted with CHCl<sub>3</sub> (3 × 25 mL). The organic layers were combined, and washed with water (20 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated *in vacuo* to give the crude product. The crude product was purified by column chromatography using hexane: ethylacetate (9:1–6:4%) as eluent to afford the pure product.

#### 2.4 General procedure for the synthesis of *N*-( $\omega$ -azidoalkyl)-1,8-naphthalimide (IXa-f)

One equivalent of *N*-( $\omega$ -bromoalkyl)-1,8-naphthalimide (VIII<sub>a-f</sub>) was dissolved in DMF mix and two equivalents of sodium azide were added to it. The mixture was stirred at 80°C for 12 h. After completion of the reaction, DMF was removed *in vacuo* and poured into ice cold water, extracted with chloroform. After evaporation of chloroform, the pure compound was collected.

#### 2.5 General procedure for the synthesis of *N*-( $\omega$ -bromoalkyl)-1,8-naphthalimide (VIIIa-f)

To a solution compound VI (0.5 gm, 1 mmol) in acetonitrile (30 mL), anhydrous potassium carbonate (553 mg, 4 mmol) and terminal dibromoalkane (561 mg, 3 mmol) were added and the mixture was refluxed for 12 h. After completion of the reaction, anhydrous potassium carbonate was removed by filtration and the solvent was evaporated under reduced pressure to get the crude product. This was further purified by column chromatography (10% EtOAc-hexane) to afford the compound VIII a–f.

#### 2.6 Synthesis of 1*H*-benzo [*de*]isoquinoline-1,3(2*H*)-dione (VI)

1,8-Naphthalic anhydride (V) (1 g, 5.07 mmol) was taken in ammonia solution (60 mL) and stirred at 100°C for 12 h. After cooling, a yellowish solid was obtained, to this 200 mL of ice cold water was added and filtered at pump. The solid product was dried in oven at 100°C. The compound is characterized by IR, <sup>1</sup>HNMR and mass spectra.

#### 2.7 Spectral data

2.7a 1*H*-benzo [*de*]isoquinoline-1,3(2*H*)-dione (VI): Yield 91.7%; M.p. 262–264°C; IR (KBr): 3440, 3059, 1701, 1676, 1622, 1586 cm<sup>-1</sup>. <sup>1</sup>HNMR (CDCl<sub>3</sub>,

400 MHz)  $\delta$  7.79 (t, 2H), 8.45–8.43 (m, 4H), 11.71 (bs, 1H, D<sub>2</sub>O exchanged). ESI-MS: *m/z* 198[M+H]<sup>+</sup>.

2.7b 2-(4-bromobutyl)-1*H*-benzo [*de*]isoquinoline-1,3(2*H*)-dione (VIII c): Yield 88.4%; M.p. 100–103°C; IR (KBr): 3095, 1697, 1664, 1588 cm<sup>-1</sup>. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz): 1.87–2.03 (m 4H), 3.47 (t, 2H), 4.23 (t, 2H), 7.75 (t, *J* = 8 Hz, 2H), 8.21 (d, *J* = 8.4 Hz, 2H), 8.60 (d, *J* = 7.2 Hz, 5H). <sup>13</sup>CNMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  164.15, 133.96, 131.54, 131.25, 128.10, 126.93, 122.53, 39.34, 33.18, 30.25, 26.89. ESI-MS: *m/z* 332 [M+H]<sup>+</sup>.

2.7c 2-(5-bromopentyl)-1*H*-benzo [*de*]isoquinoline-1,3(2*H*)-dione (VIII d): Yield 87.2%; M.p. 118–120°C; IR (KBr): 3060, 2954, 1695, 1660, 1589, 1512 cm<sup>-1</sup>. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.58–1.63 (m, 2H), 1.75–1.83 (m, 2H), 1.93–2.00 (m, 2H), 3.45 (t, *J* = 6.8 Hz, 2H), 4.21 (t, *J* = 7.6 Hz, 2H), 7.78 (t, *J* = 7.6 Hz, 2H), 8.23 (d, *J* = 8.0 Hz, 2H), 8.62 (d, *J* = 7.4 Hz, 2H). ESI-MS: *m/z*: 346 [M+H]<sup>+</sup>.

2.7d 2-(6-bromohexyl)-1*H*-benzo [*de*]isoquinoline-1,3(2*H*)-dione (VIII e): Yield 85.8%; M.p. 90–94°C; IR (KBr): 3061, 2954, 2932, 1694, 1662, 1587, 1512 cm<sup>-1</sup>. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.41–1.59 (m, 4H), 1.69–1.79 (m, 2H), 1.84–1.93 (m, 2H), 3.37 (t, *J* = 6.79 Hz, 2H), 4.14 (t, *J* = 7.6 Hz, 2H), 7.73 (t, *J* = 7.93 Hz, 2H), 8.16 (d, *J* = 8.03 Hz, 2H), 8.55 (d, *J* = 7.36 Hz, 2H). <sup>13</sup>CNMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  = 26.39, 28.01, 32.87, 33.28, 40.33, 123.19, 126.92, 128.44, 131.10, 133.65, 164.14. ESI-MS: *m/z* 360 [M+H]<sup>+</sup>.

2.7e 2-(8-bromooctyl)-1*H*-benzo [*de*]isoquinoline-1,3(2*H*)-dione (VIII f): Yield 80.6%; M.p. 70–75°C; IR (KBr): 3061, 2934, 1697, 1661, 1588, 1510 cm<sup>-1</sup>. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.30–1.44 (m, 8H), 1.69–1.77 (m, 2H), 1.80–1.87 (m, 2H), 3.39 (t, *J* = 6.8 Hz, 2H), 4.17 (t, *J* = 7.6 Hz, 2H), 7.75 (t, *J* = 7.2 Hz, 2H), 8.20 (d, *J* = 8.0 Hz, 2H), 8.59 (d, *J* = 7.2 Hz, 2H). <sup>13</sup>CNMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  26.93, 28.01, 28.06, 28.55, 29.02, 32.77, 33.58, 40.34, 122.91, 126.82, 128.20, 131.02, 131.63, 133.61, 164.06. ESI-MS: *m/z* 374 [M+H]<sup>+</sup>.

2.7f *N*-( $\omega$ -azidoalkyl)-1,8-naphthalimide (IXb): M.p. 128°C; <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  2.09 (m, 2H), 3.45 (t, *J* = 6.8 Hz, 2H), 4.36 (t, *J* = 6.4 Hz, 2H), 7.78 (t, *J* = 7.6 Hz, 2H), 8.23 (dd, *J*<sup>1</sup> = 1.2 Hz, *J* = 8.4 Hz,

2H), 8.61 (dd,  $J^1 = 0.8$  Hz,  $J = 7.2$  Hz, 2H). ESI-MS:  $m/z$  303 [M+Na]<sup>+</sup>.

2.7g 2-(2-(4((naphthalen-1-yloxy)methyl)-1H-1,2,3-triazol-1-yl)ethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (IV<sub>1-a</sub>): M.p. 166–168°C; IR (KBr): 3067, 2958, 2871, 1991, 1953, 1908, 1698, 1652, 1623, 1588, 1512, 1438, 1406, 1380, 1347, 1321, 1260, 1234, 1177, 1144, 1079, 1032 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  4.1(t,  $J = 6.8$  Hz, 2H), 4.8 (t,  $J = 6$  Hz, 2H), 4.9 (s, 2H), 6.8 (d,  $J = 7.6$  Hz, 1H), 6.9 (d,  $J = 7.2$  Hz, 1H), 7.5(t,  $J = 2$  Hz, 2H), 7.8 (t,  $J = 7.6$  Hz, 2H), 8.1 (t,  $J = 6$  Hz, 1H), 8.2 (s, 1H), 8.3 (d,  $J = 6$  Hz, 2H), 8.4 (d,  $J = 7.6$  Hz, 2H), 8.4 (d,  $J = 7.2$  Hz, 2H). <sup>13</sup>CNMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  40.17, 42.38, 60.02, 110.90, 111.71, 122.41, 122.81, 125.68, 126.78, 127.96, 129.41, 131.03, 131.38, 131.92, 133.92, 135.78, 136.75, 139.30, 139.52, 147.92, 158.21, 164.41. ESI-MS:  $m/z$  449 [M+H]<sup>+</sup>.

2.7h 2-(3-(4((naphthalen-1-yloxy)methyl)-1H-1,2,3-triazol-1-yl)propyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (IV<sub>1-b</sub>): M.p. 76–78°C; IR (KBr): 3441, 3163, 3053, 2946, 2870, 2600, 2508, 2413, 2265, 2094, 1957, 1871, 1776, 1701, 1656, 1580, 1509, 1460, 1386, 1340, 1270, 1237, 1155, 1097, 1052 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  2.5(m, 2H), 4.81(t,  $J = 6.8$  Hz, 2H), 4.5 (t,  $J = 7.2$  Hz, 2H) 5.3 (s, 2H), 7.1 (d,  $J = 7.2$  Hz, 1H), 7.4 (d,  $J = 7.2$  Hz, 1H), 7.5(t,  $J = 2$  Hz, 2H), 7.8 (t,  $J = 7.6$  Hz, 2H), 8.1 (t,  $J = 6$  Hz, 1H), 8.3 (d,  $J = 6$  Hz, 2H), 8.3 (s, 1H), 8.4 (d,  $J = 8.4$  Hz, 2H), 8.5(d,  $J = 6.8$  Hz, 2H). <sup>13</sup>CNMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  30.42, 52.94, 54.51, 67.03, 110.99, 111.07, 125.51, 126.79, 127.36, 129.53, 129.65, 130.13, 130.50, 131.35, 131.66, 132.65, 135.87, 136.47, 139.25, 139.46, 147.93, 158.74, 168.78. ESI-MS:  $m/z$  462 [M+H]<sup>+</sup>.

2.7i 2-(4-(4((naphthalen-1-yloxy)methyl)-1H-1,2,3-triazol-1-yl)butyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (IV<sub>1-c</sub>): M.p. 78–80°C; IR (KBr): 3142, 3059, 2921, 2852, 1716, 1615, 1509, 1441, 1390, 1268, 1238, 1147, 1097, 1070 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  1.8(m, 2H), 2.1(m, 2H), 4.0 (t,  $J = 6$  Hz, 2H) 4.4 (t,  $J = 6.8$  Hz, 2H), 5.4 (s, 2H), 6.1(s, 1H), 6.8 (m, 2H), 6.9(d,  $J = 7.6$  Hz, 1H), 7.4 (m, 5H), 7.7 (s, 1H), 7.8(d,  $J = 7.6$  Hz, 1H), 8.0 (s, 1H), 8.2 (d,  $J = 8$  Hz, 2H). <sup>13</sup>CNMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  25.99, 27.00, 31.93, 50.07, 67.42, 101.27, 105.38, 111.85, 112.38, 113.58, 120.82, 121.96, 125.27, 125.56, 125.62,

125.86, 126.48, 127.49, 134.49, 152.67, 153.91, 155.11, 161.25, 161.69. ESI-MS:  $m/z$  477 [M+H]<sup>+</sup>.

2.7j 2-{5-[4(naphthalen-1-yloxymethyl)-[1,2,3]triazol-1-yl]pentyl}-benzo[de]isoquinoline-1,3-dione (IV<sub>1-d</sub>): M.p. 108–110°C; IR (KBr): 3141, 3057, 2951, 2872, 2598, 2119, 1957, 1873, 1778, 1697, 1658, 1591, 1509, 1437, 1342, 1240, 1154, 1067 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  = 1.3 (m, 2H) 1.7(m, 2H), 1.9(m, 2H), 4.0 (t,  $J = 7.6$  Hz, 2H), 4.4 (t,  $J = 7.2$  Hz, 2H), 5.3 (s, 2H), 7.0 (d,  $J = 7.2$  Hz, 1H), 7.1 (d,  $J = 7.2$  Hz, 1H), 7.4(t,  $J = 8.4$  Hz, 1H), 7.5 (t,  $J = 2.4$  Hz, 2H), 7.8 (t,  $J = 8.4$  Hz, 2H), 8.12 (d,  $J = 8$  Hz, 2H), 8.3 (s, 1H), 8.4(d,  $J = 8$  Hz, 2H), 8.5 (d,  $J = 7.2$  Hz, 2H). <sup>13</sup>CNMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  28.62, 32.13, 34.65, 54.49, 61.08, 67.00, 83.66, 110.96, 125.50, 125.86, 127.12, 130.50, 130.70, 131.15, 131.33, 132.31, 132.45, 132.64, 132.72, 135.85, 136.40, 139.23, 139.42, 158.70, 168.52. ESI-MS:  $m/z$  491 [M+H]<sup>+</sup>.

2.7k 2-(6-(4((naphthalen-1-yloxy)methyl)-1H-1,2,3-triazol-1-yl)hexyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (IV<sub>1-e</sub>): M.p. 98–100°C; IR (KBr): 3058, 3012, 2938, 2861, 1697, 1658, 1625, 1587, 1508, 1460, 1440, 1390, 1346, 1268, 1236, 1175, 1098, 1069, 1021 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  = 1.2 (m, 2H) 1.3 (m, 2H), 1.6 (m, 2H), 1.8 (m, 2H) 4.0 (t,  $J = 7.2$  Hz, 2H), 4.4 (t,  $J = 6.8$  Hz, 2H), 5.3 (s, 2H), 7.1 (d,  $J = 6.8$  Hz, 1H), 7.4(t,  $J = 8.0$  Hz, 1H), 7.1 (t,  $J = 2.4$  Hz, 2H), 7.8 (t,  $J = 8.0$  Hz, 2H), 8.1 (d,  $J = 8.4$  Hz, 2H), 8.1 (d,  $J = 8.4$  Hz, 1H), 8.3(s, 1H), 8.4 (d,  $J = 8.0$  Hz, 2H), 8.4 (d,  $J = 7.2$  Hz, 2H). <sup>13</sup>CNMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  27.33, 27.55, 30.00, 31.12, 54.81, 60.94, 66.98, 110.37, 125.36, 125.42, 125.74, 126.61, 126.79, 127.20, 130.06, 130.20, 130.71, 131.38, 132.30, 132.64, 135.71, 136.33, 138.99, 139.14, 139.17, 158.70. ESI-MS:  $m/z$  505 [M+H]<sup>+</sup>.

2.7l 2-{8-[4(naphthalen-1-yloxymethyl)-[1,2,3]triazol-1-yl]octyl}benzo[de]isoquinoline-1,3-dione (IV<sub>1-f</sub>): M.p. 78–80°C; IR (KBr): 3050, 2929, 2851, 2599, 2417, 2118, 1968, 1914, 1872, 1786, 1698, 1662, 1591, 1508, 1438, 1345, 1267, 1238, 1154, 1098, 1051 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  1.2 (m, 8H) 1.6 (m, 2H), 1.8 (m, 2H), 4.0 (t,  $J = 7.6$  Hz, 2H) 4.3 (t,  $J = 7.2$  Hz, 2H), 5.3 (s, 2H), 7.0 (d,  $J = 7.6$  Hz, 1H), 7.1 (d,  $J = 7.6$  Hz, 1H), 7.4(t,  $J = 2.4$  Hz, 1H), 7.5 (t,  $J = 2.4$  Hz, 2H), 7.8 (t,  $J = 7.6$  Hz, 2H), 8.1 (d,  $J = 8.4$  Hz, 2H), 8.3 (s, 1H), 8.4(d,  $J = 7.6$  Hz, 2 H), 8.4 (d,  $J = 7.2$  Hz, 2H). <sup>13</sup>CNMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  31.02, 31.63, 32.65, 33.46, 33.73, 34.92, 54.79,

60.95, 66.96, 110.41, 125.36, 125.74, 126.79, 127.24, 130.09, 130.19, 130.29, 130.91, 131.32, 131.87, 132.30, 132.64, 135.71, 136.36, 139.02, 139.16, 158.70, 168.49. ESI-MS:  $m/z$  533 [M+H]<sup>+</sup>

2.7m 2-(2-(4((4-methoxynaphthalen-1-yloxy)methyl)-1H-1,2,3-triazol-1-yl)ethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (IV<sub>2-a</sub>): M.p. 120–122°C; IR (KBr): 2923, 2853, 1696, 1658, 1624, 1591, 1462, 1440, 1381, 1344, 1272, 1236, 1152, 1095, 1048 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  3.6 (d,  $J = 4.4$ , 2H), 3.9 (s, 3H), 4.1 (d,  $J = 6.8$  Hz, 2H), 4.9 (s, 2H), 6.8 (d,  $J = 7.6$  Hz, 1H), 6.9 (d,  $J = 7.2$  Hz, 1H), 7.5 (t,  $J = 2$  Hz, 2H), 7.8 (t,  $J = 7.6$  Hz, 2H), 8.1 (d,  $J = 6$  Hz, 2H), 8.2 (s, 1H), 8.4 (d,  $J = 7.6$  Hz, 2H), 8.4 (d,  $J = 6$  Hz, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  47.03, 60.45, 61.28, 63.58, 107.92, 110.61, 122.41, 125.68, 126.47, 126.59, 127.42, 129.41, 130.68, 130.85, 131.00, 131.82, 132.80, 135.71, 136.36, 138.93, 151.75, 154.56, 168.83. ESI-MS:  $m/z$  479 [M+H]<sup>+</sup>.

2.7n 2-(3-(4((4-methoxynaphthalen-1-yloxy)methyl)-1H-1,2,3-triazol-1-yl)propyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (IV<sub>2-b</sub>): M.p. 58–60°C; IR (KBr): 3076, 2949, 2861, 2725, 2598, 2002, 1979, 1880, 1695, 1655, 1588, 1442, 1389, 1348, 1272, 1236, 1172, 1096, 1057 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  2.5 (m, 2H), 3.5 (t,  $J = 6.4$  Hz, 2H), 3.9 (s, 3H), 4.1 (t,  $J = 7.6$ , 2H), 5.3 (s, 2H), 7.1 (d,  $J = 7.2$  Hz, 1H), 7.4 (d,  $J = 7.2$  Hz, 1H), 7.5 (t,  $J = 2$  Hz, 2H), 7.8 (t,  $J = 7.6$  Hz, 2H), 8.3 (d,  $J = 6$  Hz, 2H), 8.3 (s, 1H), 8.4 (d,  $J = 8.4$  Hz, 2H), 8.5 (d,  $J = 7.2$  Hz, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  27.26, 39.58, 42.76, 54.55, 64.22, 104.25, 104.38, 110.90, 111.15, 125.45, 126.60, 129.60, 130.25, 131.27, 132.33, 132.45, 135.81, 136.41, 139.39, 139.45, 147.90, 158.46, 168.55. ESI-MS:  $m/z$  493 [M+H]<sup>+</sup>.

2.7o 2-(4-(4((4-methoxynaphthalen-1-yloxy)methyl)-1H-1,2,3-triazol-1-yl)butyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (IV<sub>2-c</sub>): M.p. 63–65°C; IR (KBr): 3074, 2939, 2873, 2498, 2403, 2095, 1954, 1716, 1614, 1510, 1462, 1388, 1272, 1146, 1071 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  1.7 (m, 2H), 2.0 (m, 2H), 3.9 (s, 3H), 4.1 (t,  $J = 1.6$  Hz, 2H), 4.4 (t,  $J = 1.6$  Hz, 2H), 5.2 (s, 2H), 6.1 (s, 1H), 6.8 (d,  $J = 8.4$  Hz, 1H), 6.9 (m, 3H), 7.0 (d,  $J = 8.8$  Hz, 1H), 7.5 (t,  $J = 3.6$  Hz, 2H), 7.6 (d,  $J = 8.8$  Hz, 2H), 8.1 (d,  $J = 2$  Hz, 2H), 8.3 (s, 1H), 8.3 (s, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  23.32, 30.91, 31.68, 54.29, 60.74, 67.30, 106.31, 108.83, 110.92, 116.31, 117.55, 118.26, 126.60, 126.75, 130.95,

131.03, 131.06, 131.52, 152.56, 154.17, 158.47, 159.93, 165.34, 166.77, 166.81. ESI-MS:  $m/z$  507 [M+H]<sup>+</sup>.

2.7p 2-(5-(4((4-methoxynaphthalen-1-yloxy)methyl)-1H-1,2,3-triazol-1-yl)pentyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (IV<sub>2-d</sub>): M.p. 108–110°C; IR (KBr): 3131, 3067, 2947, 2853, 1950, 1781, 1696, 1658, 1592, 1463, 1388, 1272, 1237, 1099, 1049 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  1.3 (m, 2H), 1.7 (m, 2H), 1.9 (m, 2H), 3.9 (s, 3H), 4.0 (t,  $J = 7.2$  Hz, 2H), 4.4 (t,  $J = 6.8$  Hz, 2H), 5.2 (s, 2H), 6.8 (d,  $J = 8.4$  Hz, 1H), 7.0 (d,  $J = 8.4$  Hz, 1H), 7.5 (t,  $J = 4$  Hz, 2H), 7.8 (t,  $J = 7.2$  Hz, 2H), 8.0 (d,  $J = 1.6$  Hz, 2H), 8.3 (s, 1H), 8.4 (d,  $J = 8.4$  Hz, 4H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  28.61, 32.12, 34.65, 54.46, 60.76, 61.35, 67.29, 108.89, 110.91, 126.57, 126.64, 126.77, 127.14, 130.68, 130.91, 131.07, 131.10, 131.28, 132.33, 132.47, 135.86, 136.41, 139.43, 152.54, 154.13, 168.53. ESI-MS:  $m/z$  521 [M+H]<sup>+</sup>.

2.7q 2-(6-(4((4-methoxynaphthalen-1-yloxy)methyl)-1H-1,2,3-triazol-1-yl)hexyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (IV<sub>2-e</sub>): M.p. 98–100°C; IR (KBr): 3069, 2934, 2859, 2599, 2423, 2309, 1959, 1699, 1657, 1591, 1463, 1439, 1387, 1272, 1237, 1098, 1078, 1023 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  1.3 (m, 2H), 1.3 (m, 2H), 1.6 (m, 2H), 1.8 (m, 2H), 3.9 (s, 3H), 4.0 (t,  $J = 7.2$  Hz, 2H), 4.4 (t,  $J = 6.8$  Hz, 2H), 5.2 (s, 2H), 6.8 (d,  $J = 8.4$  Hz, 1H), 7.0 (d,  $J = 8.4$  Hz, 1H), 7.4 (t,  $J = 3.2$  Hz, 2H), 7.8 (t,  $J = 7.2$  Hz, 2H), 8.0 (d,  $J = 2.4$  Hz, 2H), 8.3 (s, 1H), 8.4 (d,  $J = 8.4$  Hz, 2H), 8.5 (d,  $J = 6.4$  Hz, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  30.76, 31.12, 32.52, 34.77, 54.69, 60.56, 61.37, 67.40, 108.35, 108.47, 110.64, 110.96, 126.52, 126.69, 127.21, 129.52, 130.72, 130.78, 131.02, 132.01, 132.60, 135.75, 136.41, 139.18, 152.59, 154.21, 168.47. ESI-MS:  $m/z$  535 [M+H]<sup>+</sup>.

2.7r 2-(8-(4((4-methoxynaphthalen-1-yloxy)methyl)-1H-1,2,3-triazol-1-yl)octyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (IV<sub>2-f</sub>): M.p. 108–110°C; IR (KBr): 2919, 2851, 1697, 1659, 1592, 1462, 1386, 1345, 1271, 1237, 1156, 1096, 1024 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  1.2 (m, 8H), 1.6 (m, 2H), 1.8 (m, 2H), 3.9 (s, 3H), 4.0 (t,  $J = 7.6$  Hz, 2H), 4.3 (t,  $J = 7.2$  Hz, 2H), 5.2 (s, 2H), 6.8 (d,  $J = 8.4$  Hz, 1H), 7.0 (d,  $J = 8.4$  Hz, 1H), 7.4 (t,  $J = 0.8$  Hz, 2H), 7.8 (t,  $J = 7.6$  Hz, 2H), 8.0 (d,  $J = 4.8$  Hz, 2H), 8.3 (s, 1H), 8.4 (d,  $J = 8.0$  Hz, 2H), 8.4 (d,  $J = 6.8$  Hz, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  30.97, 31.62, 32.60, 33.41, 33.73,

34.86, 54.57, 60.75, 67.29, 108.87, 110.95, 111.27, 126.56, 126.74, 127.20, 129.50, 130.67, 130.92, 131.04, 131.08, 131.29, 132.37, 132.49, 135.88, 136.45, 139.45, 152.51, 154.12, 168.54. ESI-MS: $m/z$  563  $[M+H]^+$ .

### 3. Results and discussion

The present investigation focuses on the development of a few triazolophthalenes starting from 1-naphthol. The synthetic chemistry employed to prepare the target compounds is outlined in scheme 1. Regioselective synthesis of 1, 2, 3-triazole-substituted bisnaphtholotriazoles involves three steps: (1) Propargylation of naphthol, (2) Synthesis of alkyl azides (scheme 2) and (3) Click reaction of propargylated naphthols with azides (scheme 1 and table 1).

Naphthols II-2 on reaction with propargyl bromide in presence of  $K_2CO_3$  give propargylatednaphthyl ethers III-2. The structure of naphthylether was confirmed by appearance of propargylic and terminal alkyne protons at  $\delta$  2.5 and 4.8 in the  $^1H$  NMR spectrum. The IR spectra of these compounds exhibited a new weak absorption maximum at around  $2100\text{ cm}^{-1}$  characteristic of  $\lambda_{C\equiv C}$  stretching indicating the formation of propargylated naphthol ethers III 1-2.

N-( $\omega$ -bromo)alkyl)-1,8-naphthalimides (VIII<sub>a-f</sub>) were freshly generated by the reaction of naphthalimide with appropriate alkyldibromides in acetonitrile and anhydrous potassium carbonate with good yields. Completion of the reaction was monitored by thin layer chromatography.

N-( $\omega$ -Azido)alkyl)-1,8-naphthalimides (IX<sub>a-f</sub>) were freshly prepared by the reaction of appropriate N-( $\omega$ -bromo)alkyl)-1,8-naphthalimide (VIII<sub>a-f</sub>) with sodium azide in DMF with good yields.

The final step of the synthesis was the click reaction. Propargylic ethers of naphthalols (III-2) react with azidonaphthalimides (IX<sub>a-f</sub>) in presence of aq.  $CuSO_4 \cdot 5H_2O$  and aq. sodium ascorbate in DMF to give 1,4-disubstituted naphthyloxy methyl-N-

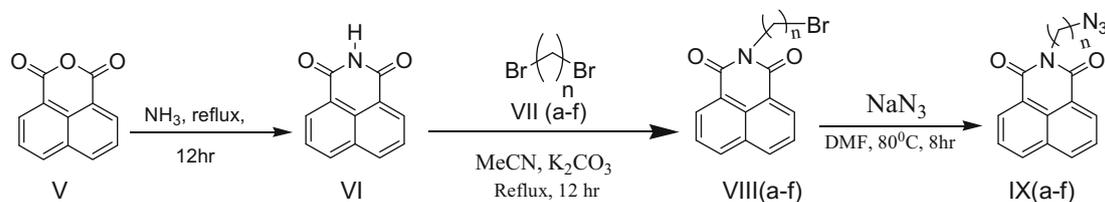
alkyl naphthimido-1,2,3-triazoles (IV1-2a-f) in excellent yields. The structures of all compounds were characterized by  $^1H$ ,  $^{13}C$  NMR spectra and mass spectra. Formation of triazole ring was unequivocally established by the characteristic chemical shift value of the triazolyl proton resonated at  $\delta$  8.07–8.54 ppm. Triazole ring formation can also be confirmed by  $^{13}C$ -spectra with the new signals of the olefinic C-atoms of the 1,2,3-triazole moiety at  $\delta$  122.5–127 ppm and  $\delta$  139–148.

#### 3.1 Electronic spectral study of 1,4-disubstituted naphthyloxy methyl N-alkyl naphthimido-1,2,3-triazoles

Formation of 1,2,3-triazole moiety extended the aromatic conjugation between electron donor and electron acceptor molecules. It was demonstrated that 1,4-disubstituted triazoles give enhanced spectral properties when triazole ring extends the aromatic delocalization from the donor moiety to the acceptor through intramolecular charge transfer phenomena 1,2,5. If it is assumed that when the triazole is placed in between two aromatic chromophores and prevent the conjugation by introducing  $sp^3$ -hybridized atoms then the resulting molecule may yield no better spectral properties. The 1,4-disubstituted naphthoxymethyl-N-alkyl naphthalimide-1,2,3-triazoles reported in this study possess no possibility for the electron delocalization from naphthyl to naphthalimide or vice versa via 1,2,3-triazole ring due to the presence of  $sp^3$ -hybridized linker atoms such as oxygen, nitrogen and carbon. It is therefore interesting to investigate the electronic absorption and emission properties in order to evaluate aromatic conjugation from one end to another (figure 1).

#### 3.2 Electronic absorption spectral study

Electronic absorption spectra of IV 2c, IV 2d and IV 2e in DMF are shown in figure 1. Similarly, electronic



Where n = 2-a, 3-b, 4-c, 5-d, 6-e, 8-f.

**Scheme 2.** Synthesis of azidonaphthalimides.

**Table 1.** Synthesis of 1,4-disubstituted naphthoxyethyl-N-alkyl naphthimido-1,2,3-triazoles.

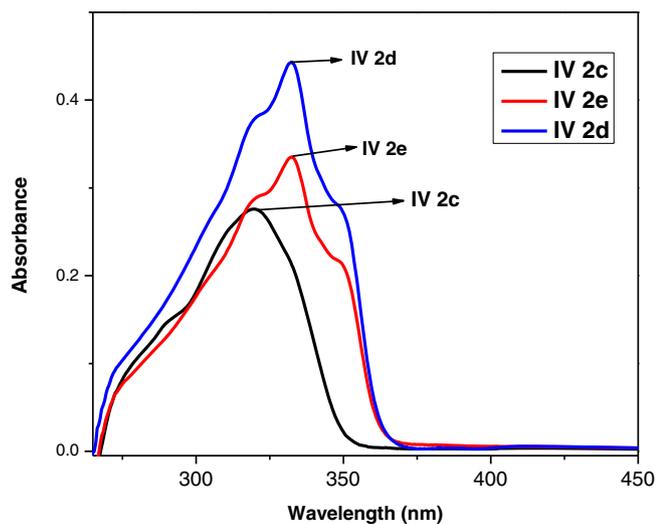
S. no.	Compound	R	N	Time (h)	Yield (%)
1	IV 1a	H	2	12.0	82
2	IV 1b	H	3	12.0	86
3	IV 1c	H	4	12.0	92
4	IV 1d	H	5	12.0	89
5	IV 1e	H	6	12.0	74
6	IV 1f	H	8	12.0	88
7	IV 2a	OCH <sub>3</sub>	2	12.0	90
8	IV 2b	OCH <sub>3</sub>	3	12.0	79
9	IV 2c	OCH <sub>3</sub>	4	12.0	82
10	IV 2d	OCH <sub>3</sub>	5	12.0	94
11	IV 2e	OCH <sub>3</sub>	6	12.0	90
12	IV 2f	OCH <sub>3</sub>	8	12.0	79

absorption spectra of 2-(3-(4((4-methoxynaphthalen-1-yloxy)methyl)-1H-1,2,3-triazol-1-yl)propyl)-1H-benzo [de]isoquinoline-1,3(2H)-dione, IV 2b in four different solvents are given in figure 2. Electronic absorption spectral data of all the 1,4-disubstituted naphthoxyethyl-N-alkyl naphthalimide-1,2,3-triazoles including the starting naphthols and their propargyl ethers is shown in tables 2 to 6.

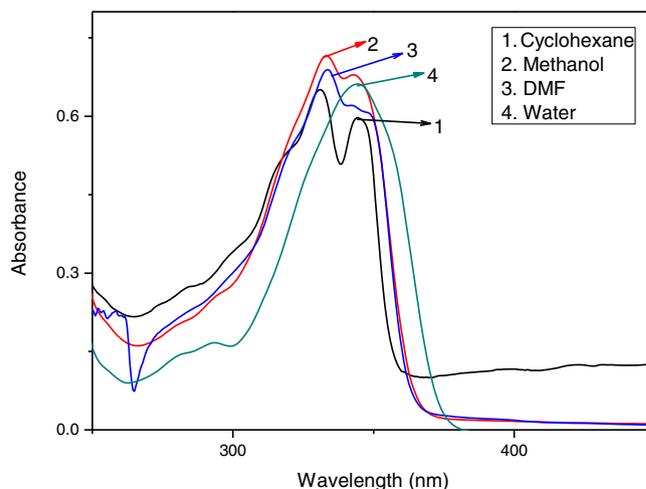
From figure 1 it can be noticed that electronic transition that occurred are due to the naphthalene aromatic ring. Further, these transitions occur due to the naphthoxy moiety. The <sup>1</sup>La transition of naphthalene occurs at longer wavelength while the <sup>1</sup>Lb transition occurred at shorter wavelength. However, from molar extinction coefficients, it can be revealed that the triazole ring contributed significantly to the spectral shifts. Attachment of triazole caused a little bathochromic shift of naphthol or naphthoxypropargyl

ether in 1,4-disubstituted naphthoxyethyl-N-alkyl naphthalimide-1,2,3-triazoles. Similarly, covalent attachment of triazolyl unit to the alkoxy carbon of naphthyl ether enhanced the absorptivity of 1,4-disubstituted naphthoxyethyl-N-alkyl naphthalimide-1,2,3-triazoles.

Examination of figure 2 reveals that absorption spectrum of the compound IV 2b in water is different from that of rest of the solvents. In water, compound IV 2b exhibited a single broad absorption maximum, while in the remaining solvents, it has given a doublet absorption maxima in the near visible region. Similar observation was found in all the 1,4-disubstituted naphthoxyethyl-N-alkyl naphthalimide-1,2,3-triazoles. On closer examination of the absorption spectral data presented in tables 2 to 6, it can be observed that there is no extensive delocalization of aromatic  $\pi$ -electrons in the 1,4-disubstituted naphthoxyethyl-N-alkyl naphthalimide-1,2,3-triazoles.



**Figure 1.** Electronic absorption spectrum of IV 2c  $1.32 \times 10^{-5}$  M, IV 2d  $1.41 \times 10^{-5}$  M and IV 2e  $1.06 \times 10^{-5}$  M in DMF.



**Figure 2.** Electronic absorption spectrum of IV 2b  $2.08 \times 10^{-5}$  M in different solvents.

**Table 2.** Electronic absorption and fluorescence data of  $\alpha$ -naphthol, 4-methoxy naphthol, naphthylpropargylicethers, 1,4-disubstituted naphthyloxymethyl-N-alkyl naphthimido-1,2,3-triazoles in cyclohexane.

Compound	$\lambda_{\text{abs.max}}$ (nm) ( $\epsilon, \text{dm}^2 \text{mol}^{-1}$ )	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{flu.max}}$ (nm)	Stokes shift (nm)	$\Phi_f$
<b>I-1</b>	309( $4.3 \times 10^3$ ), 323( $3.53 \times 10^3$ )	369	452	83	$8 \times 10^{-6}$
<b>I-2</b>	333( $1.16 \times 10^4$ ), 369( $1.93 \times 10^3$ )	369	452	83	$2.55 \times 10^{-3}$
<b>III-1</b>	320( $4.3 \times 10^1$ ), 379( $4.2 \times 10^2$ )	369	453	84	$1.3 \times 10^{-7}$
<b>III-2</b>	307( $7.6 \times 10^3$ ), 315( $7.6 \times 10^3$ ), 330( $7.5 \times 10^3$ )	369	453	84	$3.6 \times 10^{-5}$
<b>IV 1b</b>	283( $4 \times 10^4$ ), 312( $3.7 \times 10^4$ ), 320( $3.72 \times 10^4$ ), 331( $3.71 \times 10^4$ ), 342( $3.74 \times 10^4$ ), 368( $3.25 \times 10^4$ )	369	453	84	$5.57 \times 10^{-2}$
<b>IV 1c</b>	290( $2.43 \times 10^4$ ), 309( $2.52 \times 10^4$ ), 320( $2.51 \times 10^4$ ), 345( $2.1 \times 10^4$ )	368	453	85	$2.2 \times 10^{-3}$
<b>IV 1d</b>	231( $15.7 \times 10^4$ ), 293( $4.35 \times 10^4$ ), 312( $4.13 \times 10^4$ ), 320( $4.2 \times 10^4$ ), 330( $4.3 \times 10^4$ ), 345( $4.14 \times 10^4$ )	368	453	85	$4.9 \times 10^{-2}$
<b>IV 1e</b>	232( $3.4 \times 10^4$ ), 293( $1.35 \times 10^4$ ), 306( $1.14 \times 10^4$ ), 311( $1.15 \times 10^4$ ), 320( $1.2 \times 10^4$ ), 330( $1.19 \times 10^4$ ), 345( $1.12 \times 10^4$ )	369	453	84	$3.3 \times 10^{-3}$
<b>IV 1f</b>	213( $13.2 \times 10^4$ ), 232( $13.7 \times 10^4$ ), 294( $2.7 \times 10^4$ ), 312( $2.64 \times 10^4$ ), 320( $2.78 \times 10^4$ ), 330( $2.89 \times 10^4$ ), 345( $2.8 \times 10^4$ )	368	454	86	$2.3 \times 10^{-1}$
<b>IV 2b</b>	235( $10.7 \times 10^4$ ), 331( $3.13 \times 10^4$ ), 344( $2.87 \times 10^4$ )	369	454	85	$2.6 \times 10^{-2}$
<b>IV 2c</b>	241( $1.83 \times 10^4$ ), 317( $1.54 \times 10^4$ ), 373( $4.16 \times 10^3$ )	369	452	83	$9.1 \times 10^{-2}$
<b>IV 2d</b>	317( $2.66 \times 10^4$ ), 330( $3 \times 10^4$ ), 345( $1.98 \times 10^4$ ), 381( $3 \times 10^3$ )	369	453	84	$8 \times 10^{-2}$
<b>IV 2e</b>	317( $7.95 \times 10^4$ ), 330( $8.3 \times 10^4$ ), 334( $7 \times 10^4$ )	368	453	85	$2.4 \times 10^{-2}$
<b>IV 2f</b>	318( $3.28 \times 10^4$ ), 330( $3.76 \times 10^4$ ), 344( $2.78 \times 10^4$ )	369	453	84	$6.2 \times 10^{-2}$

Absorption maxima of the title compounds lie in the range of absorption maxima of naphthol and alkylated naphthimide. It is therefore difficult to assign the light absorbing chromophore in the absence of delocalization aromatic  $\pi$ -electrons from one naphthyl ring at one

end to the other naphthyl ring at the other end via 1,2,3-triazoles. To identify the light absorbing chromophore in the 1,4-disubstituted naphthyloxymethyl-N-alkyl naphthalimide-1,2,3-triazoles, excitation and emission studies have been undertaken with spectrofluorophotometer.

**Table 3.** Electronic absorption and fluorescence data of  $\alpha$ -naphthol, 4-methoxy naphthol, naphthylpropargylicethers, 1,4-disubstituted naphthyloxymethyl-N-alkyl naphthimido-1,2,3-triazoles in chloroform.

Compound	$\lambda_{\text{abs.max}}$ (nm) ( $\epsilon, \text{dm}^2 \text{mol}^{-1}$ )	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{flu.max}}$ (nm)	Stokes shift (nm)	$\Phi_f$
<b>I-1</b>	323( $2.8 \times 10^3$ )	373	458	85	$1.74 \times 10^{-3}$
<b>I-2</b>	333( $1.12 \times 10^4$ ), 374( $1.75 \times 10^3$ )	373	460	87	$1.8 \times 10^{-3}$
<b>III-1</b>	320( $4.11 \times 10^2$ ), 352( $4.33 \times 10^1$ )	372	458	86	$4.6 \times 10^{-6}$
<b>III-2</b>	244( $4.7 \times 10^3$ ), 316( $1.29 \times 10^3$ ), 361( $2.96 \times 10^2$ )	373	459	86	$7.2 \times 10^{-5}$
<b>IV 1b</b>	295( $9 \times 10^3$ ), 307( $8.57 \times 10^3$ ), 322( $9.69 \times 10^3$ ), 336( $1.12 \times 10^4$ ), 351( $1.19 \times 10^4$ ), 373( $6.63 \times 10^3$ )	372	459	87	$1.3 \times 10^{-2}$
<b>IV 1c</b>	294( $2.68 \times 10^4$ ), 312( $3.07 \times 10^4$ ), 321( $1.35 \times 10^4$ )	395	434	39	$2.4 \times 10^{-4}$
<b>IV 1d</b>	283( $2 \times 10^4$ ), 294( $2.13 \times 10^4$ ), 307( $1.86 \times 10^4$ ), 321( $2.1 \times 10^4$ ), 334( $2.17 \times 10^4$ ), 349( $1.93 \times 10^4$ )	372	433	61	$5.7 \times 10^{-3}$
<b>IV 1e</b>	294( $1.64 \times 10^4$ ), 307( $1.37 \times 10^4$ ), 321( $1.47 \times 10^4$ ), 335( $1.49 \times 10^4$ ), 350( $1.35 \times 10^4$ )	372	457	85	$2.8 \times 10^{-3}$
<b>IV 1f</b>	295( $2.52 \times 10^4$ ), 307( $2.29 \times 10^4$ ), 321( $2.65 \times 10^4$ ), 334( $2.84 \times 10^4$ ), 349( $2.55 \times 10^4$ )	370	459	89	$9.5 \times 10^{-2}$
<b>IV 2b</b>	241( $6.29 \times 10^4$ ), 283( $1.6 \times 10^4$ ), 336( $3.85 \times 10^4$ )	372	457	85	$2.2 \times 10^{-1}$
<b>IV 2c</b>	244( $3.26 \times 10^4$ ), 320( $2.66 \times 10^4$ )	372	458	86	$4.5 \times 10^{-2}$
<b>IV 2d</b>	241( $10 \times 10^4$ ), 332( $4.3 \times 10^4$ )	372	459	87	$5.2 \times 10^{-2}$
<b>IV 2e</b>	284( $2.1 \times 10^4$ ), 332( $3.59 \times 10^4$ )	372	458	86	$4.7 \times 10^{-2}$
<b>IV 2f</b>	242( $6.7 \times 10^4$ ), 333( $3.83 \times 10^4$ )	372	457	82	$1.8 \times 10^{-2}$

**Table 4.** Electronic absorption and fluorescence data of  $\alpha$ -naphthol, 4-methoxy naphthol, naphthylpropargylicethers, 1,4-disubstituted naphthoxy methyl-N-alkynaphthimido-1,2,3-triazoles in methanol.

Compound	$\lambda_{\text{abs}\cdot\text{max}}$ (nm)( $\epsilon, \text{dm}^2 \text{mol}^{-1}$ )	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{flu}\cdot\text{max}}$ (nm)	Stokes shift (nm)	$\Phi_f$
<b>I -1</b>	232( $2.4 \times 10^4$ ), 295( $4.3 \times 10^3$ ), 323( $2.4 \times 10^3$ )	368	429	61	$4.7 \times 10^{-4}$
<b>I -2</b>	244( $4.3 \times 10^3$ ), 321( $1.1 \times 10^3$ ), 332( $1 \times 10^3$ )	368	429	61	$6 \times 10^{-5}$
<b>III -1</b>	227( $5 \times 10^3$ ), 289( $1 \times 10^3$ ), 319( $3.23 \times 10^2$ )	367	429	62	$4.3 \times 10^{-7}$
<b>III -2</b>	242( $6.2 \times 10^3$ ), 315( $1.6 \times 10^3$ ), 328( $1.4 \times 10^3$ )	369	429	60	$2.4 \times 10^{-4}$
<b>IV 1b</b>	207( $1.2 \times 10^5$ ), 230( $4.55 \times 10^4$ ), 292( $6.63 \times 10^3$ ), 306( $8.57 \times 10^3$ ), 320( $6.22 \times 10^3$ ), 343( $6.33 \times 10^3$ )	371	429	58	$2.6 \times 10^{-3}$
<b>IV 1c</b>	222( $7.76 \times 10^4$ ), 292( $2.75 \times 10^4$ ), 312( $3.13 \times 10^4$ ), 320( $3.3 \times 10^4$ )	368	428	60	$5.3 \times 10^{-4}$
<b>IV 1d</b>	210( $14.3 \times 10^4$ ), 231( $12.6 \times 10^4$ ), 291( $1.96 \times 10^4$ ), 306( $1.6 \times 10^4$ ), 320( $1.89 \times 10^4$ ), 334( $2 \times 10^4$ ), 343( $1.95 \times 10^4$ )	369	429	60	$6.6 \times 10^{-2}$
<b>IV 1e</b>	227( $3.69 \times 10^4$ ), 292( $1.6 \times 10^4$ ), 306( $1.29 \times 10^4$ ), 312( $1.23 \times 10^4$ ), 320( $1.42 \times 10^4$ ), 333( $1.44 \times 10^4$ ), 343( $1.38 \times 10^4$ )	350	429	79	$1.8 \times 10^{-3}$
<b>IV 1f</b>	214( $13.2 \times 10^4$ ), 231( $13.5 \times 10^4$ ), 293( $2 \times 10^4$ ), 306( $1.78 \times 10^4$ ), 320( $2.18 \times 10^4$ ), 333( $2.38 \times 10^4$ ), 343( $2.27 \times 10^4$ )	367	435	68	$6.5 \times 10^{-2}$
<b>IV 2b</b>	209( $9.3 \times 10^4$ ), 233( $11.8 \times 10^4$ ), 333( $3.44 \times 10^4$ ), 343( $3.27 \times 10^4$ )	347	401	54	$2.6 \times 10^{-2}$
<b>IV 2c</b>	209( $12.3 \times 10^4$ ), 242( $2 \times 10^4$ ), 318( $2.12 \times 10^4$ )	369	429	60	$2.2 \times 10^{-2}$
<b>IV 2d</b>	210( $14.4 \times 10^4$ ), 234( $9.93 \times 10^4$ ), 330( $2.97 \times 10^4$ ), 343( $2.2 \times 10^4$ )	369	428	59	$4.3 \times 10^{-2}$
<b>IV 2e</b>	209( $15.2 \times 10^4$ ), 234( $10 \times 10^4$ ), 331( $3 \times 10^4$ ), 343( $2.1 \times 10^4$ )	368	429	61	$2.3 \times 10^{-2}$
<b>IV 2f</b>	212( $9.69 \times 10^4$ ), 234( $10 \times 10^4$ ), 331( $3 \times 10^4$ ), 343( $1.2 \times 10^4$ )	369	429	60	$2.2 \times 10^{-2}$

**Table 5.** Electronic absorption and fluorescence data of  $\alpha$ -naphthol, 4-methoxy naphthol, naphthylpropargylicethers, 1,4-disubstituted naphthoxymethyl-N-alkyl naphthimido-1,2,3-triazoles in dimethylformamide.

Compound	$\lambda_{\text{abs}\cdot\text{max}}$ (nm)( $\epsilon, \text{dm}^2 \text{mol}^{-1}$ )	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{flu}\cdot\text{max}}$ (nm)	Stokes shift (nm)	$\Phi_f$
<b>I -1</b>	298( $5 \times 10^3$ ), 310( $4.27 \times 10^3$ ), 324( $3.43 \times 10^3$ )	373	434	61	$7.3 \times 10^{-6}$
<b>I -2</b>	278( $7.3 \times 10^3$ ), 322( $1.4 \times 10^4$ ), 355( $1.36 \times 10^4$ )	373	434	61	$2 \times 10^{-3}$
<b>III -1</b>	260( $6.68 \times 10^2$ ), 292( $1.1 \times 10^3$ ), 321( $3.9 \times 10^2$ )	374	434	60	$6.2 \times 10^{-7}$
<b>III -2</b>	227( $1.18 \times 10^3$ ), 317( $1.79 \times 10^3$ ), 330( $1.69 \times 10^3$ )	374	434	60	$2.7 \times 10^{-4}$
<b>IV 1b</b>	295( $6.53 \times 10^3$ ), 307( $6.5 \times 10^3$ ) 321( $6.94 \times 10^3$ ), 334( $6.73 \times 10^3$ )	372	433	61	$3.4 \times 10^{-2}$
<b>IV 1c</b>	295( $2.49 \times 10^4$ ), 312( $2.9 \times 10^4$ ), 320( $2.92 \times 10^4$ )	373	434	61	$1.5 \times 10^{-3}$
<b>IV 1d</b>	295( $1.87 \times 10^4$ ), 295( $1.7 \times 10^4$ ), 321( $1.95 \times 10^4$ ), 334( $1.98 \times 10^4$ )	372	433	61	$3.6 \times 10^{-2}$
<b>IV 1e</b>	295( $1.63 \times 10^4$ ), 295( $1.42 \times 10^4$ ), 313( $1.4 \times 10^4$ ), 321( $1.49 \times 10^4$ ), 334( $1.42 \times 10^4$ )	373	433	60	$3.5 \times 10^{-2}$
<b>IV 1f</b>	295( $2 \times 10^4$ ), 307( $2 \times 10^4$ ), 322( $2.28 \times 10^4$ ), 334( $2.39 \times 10^4$ ), 343( $2.2 \times 10^4$ )	372	434	62	$6.98 \times 10^{-2}$
<b>IV 2b</b>	333( $3.31 \times 10^4$ ), 342( $2 \times 10^4$ )	372	434	62	$7.5 \times 10^{-2}$
<b>IV 2c</b>	320( $2.09 \times 10^4$ ), 342( $5.9 \times 10^3$ )	373	433	60	$4.6 \times 10^{-2}$
<b>IV 2d</b>	322( $3.14 \times 10^4$ ), 344( $2 \times 10^4$ )	373	434	61	$4.8 \times 10^{-2}$
<b>IV 2e</b>	332( $3.2 \times 10^4$ ), 344( $2.1 \times 10^4$ )	373	433	60	$3.43 \times 10^{-2}$
<b>IV 2f</b>	332( $3.24 \times 10^4$ ), 344( $8.8 \times 10^3$ )	373	434	61	$9.4 \times 10^{-2}$

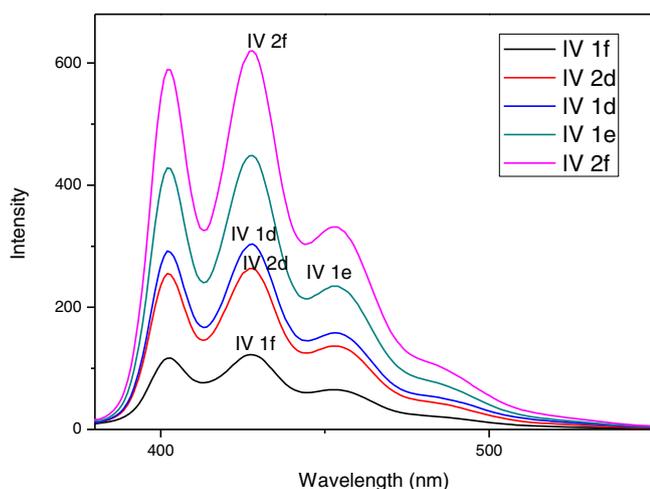
**Table 6.** Electronic absorption and fluorescence data of  $\alpha$ -naphthol, 4-methoxy naphthol, naphthylpropargylicethers, 1,4-disubstituted naphthoxyethyl-N-alkyl naphthimido-1,2,3-triazoles in water.

Compound	$\lambda_{\text{abs-max}}$ (nm)( $\epsilon, \text{dm}^2 \text{mol}^{-1}$ )	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{flu,max}}$ (nm)	Stokes shift (nm)	$\Phi_f$
I-1	291( $4 \times 10^3$ ), 321( $2 \times 10^3$ ), 361( $2.3 \times 10^2$ )	362	451	89	$1.2 \times 10^{-4}$
I-2	241( $3.78 \times 10^4$ ), 318( $9.3 \times 10^3$ ), 329( $8.77 \times 10^3$ )	374	431	57	$1.45 \times 10^{-4}$
III-1	287( $9.17 \times 10^2$ ), 319( $2.95 \times 10^2$ ), 361( $1.17 \times 10^1$ )	362	462	100	$6.3 \times 10^{-6}$
III-2	240( $4.92 \times 10^3$ ), 304( $1.29 \times 10^3$ ), 313( $1.3 \times 10^3$ )	360	413	53	$1.39 \times 10^{-4}$
IV 1b	350( $9.8 \times 10^4$ )	346	395	49	$2 \times 10^{-3}$
IV 1c	320( $1.95 \times 10^3$ )	321	384	63	$1.5 \times 10^{-4}$
IV 1d	358( $1.43 \times 10^4$ )	343	384	41	$2.5 \times 10^{-4}$
IV 1e	320( $7.3 \times 10^2$ ), 344( $7 \times 10^2$ )	344	390	46	$5.93 \times 10^{-3}$
IV 1f	348( $5.3 \times 10^1$ )	343	395	52	$1 \times 10^{-5}$
IV 2b	293( $7.8 \times 10^3$ ), 344( $3.2 \times 10^4$ )	344	384	40	$1.92 \times 10^{-4}$
IV 2c	321( $2.5 \times 10^3$ )	322	384	62	$1.32 \times 10^{-4}$
IV 2d	332( $2.13 \times 10^2$ ), 343( $1.42 \times 10^2$ )	341	386	45	$8.6 \times 10^{-5}$
IV 2e	354( $6.23 \times 10^3$ )	355	406	51	$1.99 \times 10^{-3}$
IV 2f	234( $3.68 \times 10^3$ ), 343( $1.23 \times 10^3$ )	345	392	47	$2.96 \times 10^{-4}$

### 3.3 Fluorescence study

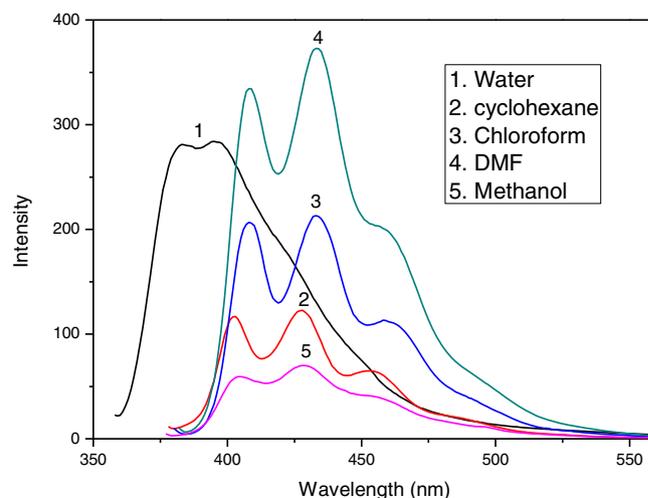
Fluorescence spectra of IV 1d, IV 1e, IV 1f, IV 2d and IV 2f in cyclohexane are given in figure 3. Similarly, fluorescence spectra of IV 1f in cyclohexane, chloroform, methanol, DMF and water are shown in figure 4. From the figure 3 it can be observed that emission spectra of IV 1f appear similar to a mirror image of its absorption spectrum.

Similar observation was made with the other compounds in all the investigated solvents. Emission data obtained in the present study is tabulated in tables 2 to 6. The light absorbing chromophore was not established



**Figure 3.** Fluorescence spectra of IV 2f  $2.6 \times 10^{-5}$  M, IV 1e  $1 \times 10^{-4}$  M, IV 1d  $9.8 \times 10^{-6}$  M, IV 2d  $1.41 \times 10^{-5}$  M and IV 1f  $1.88 \times 10^{-5}$  M in cyclohexane.

by absorption spectroscopy as both the naphthalene rings at 1,4-position of the triazole absorb in the same region. However, from the excitation and emission maxima, naphthol is the assigned light absorbing and emitting chromophore but not naphthalimide. The excitation and emission wavelength maxima in the disubstituted triazole compounds are close to that of naphthol rather than naphthalimide. The excitation and emission wavelength maxima of naphthimides are  $<340$  and  $400$  nm, respectively. However, in the present 1,4-disubstituted naphthoxyethyl-N-alkyl naphthalimide-1,2,3-triazoles, the excitation and emission maxima are in the region  $365$  to  $370$  nm and  $400$  to  $460$  nm, respectively. Therefore, the light absorbing



**Figure 4.** Fluorescence spectra of IV 1f  $1.88 \times 10^{-5}$  M in different solvents.

chromophore is the naphthol moiety rather than the naphthimide part of 1,2,3-triazole. The absorption maxima and the emission maxima of the methoxy-substituted naphthoxytriazoles (IV 2) are similar to that of the simple naphthoxy-substituted triazole (IV 1) derivatives. This is possibly due to the absence of delocalization of  $\pi$ -electrons of the positive mesomerism of methoxy group to an extent of influencing the absorption of light. Both the substituted naphthalene rings at 1,4-position of 1,2,3-triazoles are neither in conjugation with one another, nor with the triazole ring as the naphthoxy part is insulated by  $-\text{OCH}_3$  and the naphthalimide group by alkyl chain. Therefore, it can be concluded that in the absence of conjugation between the three absorbing chromophores, i.e., 1-naphthoxy, 1,2,3-triazole and naphthalimide, the light absorbing chromophore is the naphthoxy-chromophore.

The naphthoxymethylalkylimido-1,2,3-triazoles are moderately fluorescent compounds, exhibiting little solvent and substituent effects on the quantum yield and emission maxima. A closer look at tables 2 to 6 reveals that the order of quantum yield is  $\text{IV} > \text{I} 2 > \text{I} 1 > \text{III} 2 > \text{III} 1$ . A triazole ring added on to naphtholpropargyl ether improved the light emission; the methoxy substituent in naphthol also enhances the radiative emission. However, propargylation on the oxygen of 1-naphthol quenched the fluorescence. The length of the alkyl chain between the triazole and naphthimide did not bring any considerable changes in spectral properties of the 1,4-disubstituted naphthoxymethyl-N-alkyl naphthalimide-1,2,3-triazoles. Aprotic polar solvent, DMF enhanced the quantum yield while the protic polar solvents quenched the fluorescence. The effect of the solvent on the quantum yield of a given compound follows the order: DMF > cyclohexane > chloroform > methanol > water. Aqueous medium is the more quenching medium. Similarly, the effect of solvent on fluorescence emission maximum and excitation maxima is not the same for all the compounds. However, a broad generalization can be made based on the spectral data presented in the tables 2 to 6. The effect of solvent on the emission maxima varies in the order: chloroform > cyclohexane > methanol > DMF > water. The water is unique in the sense that it is the most quenching and hypsochromic medium than the remaining media. This may be due to the fact that absorption and emission maxima in water are attributed to the naphthalimide part rather than naphthol chromophore, unlike in the remaining solvents.<sup>28</sup> The Stokes shift exhibits linearity neither with the solvent polarity nor to the length of the alkyl chain, indicating that the absorbing and emitting chromophore is the naphthoxy moiety.

#### 4. Conclusions

Synthesis of a few 1,4-disubstituted naphthoxymethyl-N-alkylnaphthalimide-1,2,3-triazols is reported. The structure of these triazoles was established by spectral studies. It is proved that electronic excitation and emission techniques are superior techniques over the electronic absorption spectral technique to identify the light absorbing chromophore.  $\text{Sp}^3$ -hybridized linker atoms such as nitrogen, oxygen and carbon in between the triazole ring and the naphthalene moieties at 1,4-position prevent extensive delocalization of  $\pi$ -electrons leading to little change in the absorption and emission properties of 1,4-disubstituted naphthoxymethyl-N-alkylnaphthalimide-1,2,3-triazols when compared with 1-naphthol.

#### Supplementary information

$^1\text{H}$ ,  $^{13}\text{C}$  spectra, mass spectra, spectral data, fluorescence spectra and tables are submitted as supplementary information.

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