A new synthetic method of Gallium dodecyl sulfate (Ga (DS)$_3$)

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Abstract

α, β-unsaturated electron-deficient compounds and bis-indolylmethanes were successfully synthesized by gallium dodecyl sulfate (Ga(DS)$_3$) catalyzed Michael addition using indoles and α, β-unsaturated ketones(or aldehyde) as reactant, respectively. The samples were characterized by $^1$H NMR (400 MHz), HRMS, and Electrothermal Digital Melting-point. The results showed that the α, β-unsaturated electron-deficient compounds and bis-indolylmethanes could be effectively catalyzed by using Ga(DS)$_3$ to give the corresponding adducts in good to excellent yields in water media.

Keywords: indoles, Michael addition, α, β-unsaturated ketones, Ga(DS)$_3$

1. INTRODUCTION

Using water as the reaction solvent has attracted much attention in today’s organic chemistry. In comparison with the common organic solvent, water is cheaper and safer. And using water instead of some harmful organic solvents can lead to a development of environmentally friendly chemical processes.

Michael additions promoted by Lewis acids is one of the important carbon-carbon bond-forming reaction in organic chemistry. And indole derivatives have received a great amount of attention in recent years due to their high biological activities [1-2]. Among them 3-substituted indoles are important because of their activities and as building blocks for the synthesis of biologically active compounds and natural products [3]. Therefore, it is very important to develop new and convenient synthetic methods for them. Up to date, some methods have been reported, in which the most useful method is using Lewis acid, such as Sm [4], Ga(OTf)$_3$ [5], L$_2$ [6], Cu [7], acidic ionic liquid [8-9], Zr(NO$_3$)$_3$ [10], Cu(OTf)$_2$ [11-12], InBr$_3$ [13], InCl$_3$ [14], ZrOCl$_2$

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[15], LiBr [16-17] etc as catalyst for catalyzed the reaction of indoles and α,β-unsaturated carbonyl compounds. But some of these Lewis acids are moisture sensitive and require special care in handling and storage, and some of these examples need a long reaction time and more catalyst has to be used. Moreover, metal triflates are highly expensive. So the development of new reagents with great efficiency, convenient procedures and delivering better yields is of great interest.

In this article, we present the highly efficient Michael addition of indoles to α, β-unsaturated ketones and synthesis of bis-indolylmethanes in water media using gallium dodecyl sulfate [Ga(DS)₃] (Scheme 1) as a new Lewis acid surfactant catalyst (LASC) in water media.

2. EXPERIMENTAL

2.1. Preparation of Ga(DS)₃ from GaCl₃ and sodium dodecyl sulfate

To a stirring solution of sodium dodecyl sulfate (11.51g, 40mmol) in distilled water (300mL) was added a solution of GaCl₃ (1.76g, 10mmol) in water (75mL) at room temperature. A white precipitation appeared immediately and the mixture was stirred for another 30min. The white solid was separated by filtration and washed with water (50mL×3). The isolated solid product was dried under reduced pressure and Ga(DS)₃ as a white powder was obtained.

2.2. General procedure for preparation of α, β-unsaturated electron-deficient compounds (3a-n)

The indoles (1.0mmol), α, β-unsaturated ketones (1.2mmol) and Ga(DS)₃ (10mol%) were added to water 10mL. The mixture was stirred at 80℃ for the appropriate time (Table 1, monitored by TLC). Ethyl acetate (20mL) was added to the mixture with stirring. The organic layer was separated and dried over Na₂SO₄. Evaporation of the solvent to give the crude corresponding product. Further purification was performed by column chromatography, eluting with the appropriate solvents to give the Michael adducts in 75% to 91% isolated yield.

2.3. General procedure for preparation of bis-indolylmethanes (6a-h)

In a 20-ml round-bottom flask, a mixture of aldehyde (1 mmol) and indole (2 mmol) was stirred in the presence of Ga(DS)₃ (0.1 mmol) in water (2 ml) at 80℃ for the stipulated time (Table 2). After completion of the reaction, the product was extracted with EtOAc (3×10 ml). The organic layer was washed with brine (2×15 ml) and then water (2×10 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give a crude product. Further purification was performed by column chromatography, eluting with the appropriate solvents to give the bis-indolylmethanes.
2.4. Characterization

Melting points were recorded on an electrothermal digital melting-point apparatus and are uncorrected. 1H NMR (400 MHz) spectra were recorded on a Varian Mercury MHz spectrometer in CDCl$_3$ or DMSO-d$_6$. High-resolution mass spectra (HRMS) were obtained using a GCT-TOF instrument. IR spectra were obtained on a Nicolet FT-IR500 spectrophotometer using KBr pellets.

3. RESULTS AND DISCUSSION

Scheme 1. Chemical structural formula of Ga(DS)$_3$

In order to show the good catalytic effect of [Ga(DS)$_3$] a series of substituted indoles and α, β- unsaturated ketones were used to evaluate the scope of these Michael addition (Scheme 2). The result are summarized in Table 1. Addition of indole and indole with monosubstitution at 1-, 2-, 5-, or 7-position were studied which both obtained the desired products in good yields. From the aspect of α, β- unsaturated ketones, but-3-en-2-one, 4-methyl-3-penten-2-one and 1, 4-diaryl-α, β- unsaturated ketones all gave the corresponding adduct with the indoles in good yields (entries 1-5, 7-13). Interestingly, compound (entry 6) have two conjugated double bonds, both monoadduct and diadduct were obtained: the former was major one in a yield (81%). The structure of all the product were characterized by $^1$H NMR, $^{13}$C NMR and HRMS analyses. The structure of 3j was also characterized by X-ray single crystal diffraction (Figure 1)

Scheme 2. Ga(DS)$_3$ catalyzed the typical Michael addition reaction
Table 1. Michael addition of indoles to $\alpha, \beta$-unsaturated ketones catalyzed by Ga(DS)$_3$ in water media

<table>
<thead>
<tr>
<th>Entry</th>
<th>indoles</th>
<th>$\alpha, \beta$-unsaturated ketones</th>
<th>Product$^a$</th>
<th>t/h</th>
<th>Yield % $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image.png" alt="Indole" /></td>
<td><img src="image.png" alt="Ketone" /></td>
<td>3a</td>
<td>7</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td><img src="image.png" alt="Indole" /></td>
<td><img src="image.png" alt="Ketone" /></td>
<td>3b</td>
<td>5</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td><img src="image.png" alt="Indole" /></td>
<td><img src="image.png" alt="Ketone" /></td>
<td>3c</td>
<td>8</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td><img src="image.png" alt="Indole" /></td>
<td><img src="image.png" alt="Ketone" /></td>
<td>3d</td>
<td>8</td>
<td>83</td>
</tr>
<tr>
<td>5</td>
<td><img src="image.png" alt="Indole" /></td>
<td><img src="image.png" alt="Ketone" /></td>
<td>3e</td>
<td>6</td>
<td>89</td>
</tr>
<tr>
<td>6</td>
<td><img src="image.png" alt="Indole" /></td>
<td><img src="image.png" alt="Ketone" /></td>
<td>3f/3g</td>
<td>8</td>
<td>81/19</td>
</tr>
<tr>
<td>7</td>
<td><img src="image.png" alt="Indole" /></td>
<td><img src="image.png" alt="Ketone" /></td>
<td>3h</td>
<td>6</td>
<td>90</td>
</tr>
<tr>
<td>8</td>
<td><img src="image.png" alt="Indole" /></td>
<td><img src="image.png" alt="Ketone" /></td>
<td>3i</td>
<td>8</td>
<td>87</td>
</tr>
<tr>
<td>9</td>
<td><img src="image.png" alt="Indole" /></td>
<td><img src="image.png" alt="Ketone" /></td>
<td>3j</td>
<td>8</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td><img src="image.png" alt="Indole" /></td>
<td><img src="image.png" alt="Ketone" /></td>
<td>3k</td>
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<td>79</td>
</tr>
<tr>
<td>11</td>
<td><img src="image.png" alt="Indole" /></td>
<td><img src="image.png" alt="Ketone" /></td>
<td>3l</td>
<td>7</td>
<td>82</td>
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<td>12</td>
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<td>3m</td>
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<td>91</td>
</tr>
<tr>
<td>13</td>
<td><img src="image.png" alt="Indole" /></td>
<td><img src="image.png" alt="Ketone" /></td>
<td>3n</td>
<td>8</td>
<td>90</td>
</tr>
</tbody>
</table>

$^a$ All compounds were characterized by $^1$H NMR and HRMS spectra; $^b$ Isolated yield
Bis(indolyl)methanes are found widely distributed in the bioactive metabolites of terrestrial and marine organisms [18]. Some compounds have potent pharmaceutical activities such as tranquilizers [19] or anticarcinogen [20]. The good results above (Table 1) prompted us to explore if Ga(DS)$_3$ could also catalyze the synthesis of bis-indolylmethanes in water media. Fortunately, we found that only 10mol% Ga(DS)$_3$ can also efficiently catalyzed this reaction in water media to give exciting results (Scheme 3, Table 2)

![Scheme 3](image)

**Scheme 3.** Ga(DS)$_3$ catalyzed the typical Michael addition reaction in water media
Table 2. Ga(DS)$_3$ catalyzed synthesis of bis(indol-3-yl)methanes in water media

<table>
<thead>
<tr>
<th>Entry</th>
<th>Indole</th>
<th>Aldehyde</th>
<th>Product</th>
<th>Time</th>
<th>Yield(%)$^b$</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td><img src="image1" alt="Indole 1" /></td>
<td><img src="image2" alt="Aldehyde 1" /></td>
<td><img src="image3" alt="Product 1" /></td>
<td>3.5 h</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td><img src="image4" alt="Indole 2" /></td>
<td><img src="image5" alt="Aldehyde 2" /></td>
<td><img src="image6" alt="Product 2" /></td>
<td>2.5 h</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
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<td><img src="image8" alt="Aldehyde 3" /></td>
<td><img src="image9" alt="Product 3" /></td>
<td>3 h</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td><img src="image10" alt="Indole 4" /></td>
<td><img src="image11" alt="Aldehyde 4" /></td>
<td><img src="image12" alt="Product 4" /></td>
<td>3 h</td>
<td>87</td>
</tr>
<tr>
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<td><img src="image13" alt="Indole 5" /></td>
<td><img src="image14" alt="Aldehyde 5" /></td>
<td><img src="image15" alt="Product 5" /></td>
<td>2.5 h</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td><img src="image16" alt="Indole 6" /></td>
<td><img src="image17" alt="Aldehyde 6" /></td>
<td><img src="image18" alt="Product 6" /></td>
<td>2.5 h</td>
<td>83</td>
</tr>
<tr>
<td>7</td>
<td><img src="image19" alt="Indole 7" /></td>
<td><img src="image20" alt="Aldehyde 7" /></td>
<td><img src="image21" alt="Product 7" /></td>
<td>2.5 h</td>
<td>89</td>
</tr>
<tr>
<td>8</td>
<td><img src="image22" alt="Indole 8" /></td>
<td><img src="image23" alt="Aldehyde 8" /></td>
<td><img src="image24" alt="Product 8" /></td>
<td>2.5 h</td>
<td>60</td>
</tr>
</tbody>
</table>

$^a$ All compounds were characterized by $^1$H NMR and HRMS spectra; $^b$ Isolated yield
4. CONCLUSION

In conclusion, in this study we have introduced a new catalyst Ga(DS)$_3$, which is a green and effective combined Lewis acid surfactant catalyst for the Michael addition of indoles to structurally diverse α,β-unsaturated ketones and synthesis of bis-indolylmethanes in water media.

Spectral data of products

4-(1H-Indol-3-yl)butan-2-one (3a): M.p. 71-72°C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.98 (s, 1H, NH), 7.60-7.11 (m, 4H, C$_6$H$_4$), 6.96 (s, 1H, CH, indole ring), 3.07-3.03 (m, 2H, CH$_2$), 2.87-2.84 (m, 2H, CH$_2$), 2.13 (s, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 19.3, 30.0, 44.1, 111.1, 115.1, 118.6, 119.2, 121.4, 122.0, 127.1, 136.3, 208.8.

4-(1H-Indol-3-yl)-4-methylpentan-2-one (3b): M.p. 70-71°C. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.07 (s, 1H, NH), 7.82-7.11 (m, 4H, ArH), 6.92 (s, 1H, CH, indole ring), 2.96 (s, 2H, CH$_2$), 1.72 (s, 3H, CH$_3$), 1.54 (s, 6H, 2×CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 29.0, 34.7, 55.3, 111.9, 119.4, 120.8, 120.9, 121.9, 123.8, 125.7, 137.4, 209.8; HRMS: m/z (%) calcd. for C$_{14}$H$_{18}$NO (M$^+$) 216.1388, found 216.1380 (M$^+$, 20.08).

3-(Benzo[d][1,3]dioxol-5-yl)-3-(1H-indol-3-yl)-1-phenylpropan-1-one (3c): M.p. 130-131°C. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.01 (s, 1H, NH), 7.94-6.79 (m, 11H, ArH), 6.79 (s, 1H, indole ring), 6.71-6.68 (m, 1H, ArH), 5.85 (m, 2H, CH$_2$), 4.98 (m, 1H, CH), 3.79-3.63 (m, 2H, CH$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 38.4, 45.7, 101.3, 108.5, 108.8, 111.6, 119.8, 119.9, 121.2, 121.6, 122.6, 126.9, 129.1, 133.6, 137.0, 137.4, 138.7, 148.0, 199.0. HRMS: m/z (%) calcd. for C$_{24}$H$_{19}$NO$_3$ (M$^+$) 369.1359, found 369.1356 (M$^+$ 25.81).

1-(4-Chlorophenyl)-3-(furan-2-yl)-3-(1H-indol-3-yl)propan-1-one (3d): M.p. 61-62°C. $^1$H NMR (400MHz, CDCl$_3$): δ 8.03 (s, 1H, NH), 7.86-7.06 (m, 10H, ArH), 6.26 (s, 1H, CH), 6.06 (s, 1H, CH), 5.11 (m, 1H, CH), 3.86-3.62 (m, 2H, CH$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 32.4, 43.2, 105.9, 110.5, 111.5, 116.6, 119.5, 119.8, 122.3, 122.4, 126.3, 129.1, 129.8, 135.4, 136.6, 139.7, 141.5, 156.8, 197.3. HRMS: m/z (%) calcd. for C$_{21}$H$_{16}$NO$_2$Cl (M$^+$) 349.0870, found 349.0842 (M$^+$, 94.25).
3-(1H-Indol-3-yl)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (3e): M.p. 124-125 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.98 (s, 1H, NH), 7.94-6.99 (m, 11H, ArH), 6.96 (s, 1H, CH, indole ring), 6.81-6.70 (m, 2H, ArH), 5.01 (m, 1H, CH), 3.81-3.66 (m, 5H, CH₂+CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 126.2, 127.9, 128.4, 128.9, 130.1, 135.1, 135.5, 138.3, 144.9, 197.5. HRMS: m/z (%) cald. for C₂₄H₂₁NO₂ (M⁺) 355.1594, found 355.1580 (M⁺, 43.28).

5-(1H-Indol-3-yl)-1,5-diphenylpent-1-en-3-one (3f): M.p. 160-161 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.01 (s, 1H, NH), 7.95-6.79 (m, 14H, ArH), 6.70 (d, 1H, J = 8Hz, CH), 5.87-5.85 (m, 2H, CH=CH), 5.00 (m, 1H, CH), 3.79-3.63 (m, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 38.4, 45.7, 101.3, 108.6, 108.8, 111.6, 119.8, 119.9, 112.1, 121.6, 122.6, 126.9, 128.6, 129.1, 133.6, 137.0, 137.4, 138.7, 148.0, 199.0. HRMS: m/z (%) cald. for C₂₅H₂₁NO (M⁺) 351.1580, found 351.1579 (M⁺, 19.88).

1,5-Di(1H-indol-3-yl)-1,5-diphenylpentan-3-one (3g): M.p. 60-61 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.84 (s, 1H, NH), 7.82 (s, 1H, NH), 7.95-6.99 (m, 18H, ArH), 6.69 (s, 1H, CH, indole ring), 6.64 (s, H, CH, indole ring). 4.78 (m, 2H, 2CH), 3.24-3.02 (m, 4H, 2CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 38.4, 50.1, 111.6, 115.7, 119.1, 119.9, 122.0(2C), 122.5, 126.7, 128.1, 128.2, 128.8, 138.9, 144.3, 231.9. HRMS: m/z (%) cald. for C₃₃H₂₈N₂O (M⁺) 468.2202, found 468.2224 (M⁺, 100).

4-(5-Bromo-1H-indol-3-yl)butan-2-one (3h): M.p. 70-71 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.04 (s, 1H, NH), 7.70-7.20 (m, 3H, ArH), 6.96 (s, 1H, CH, indole ring), 3.01-2.96 (m, 2H, CH₂), 2.84-2.79 (m, 2H, CH₂), 2.14 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 19.5, 30.6, 44.3, 112.3, 113.1, 115.3, 121.7, 123.3, 125.3, 129.4, 135.3, 209.0.

3-(5-Bromo-1H-indol-3-yl)-1-(4-chlorophenyl)-3-phenylpropan-1-one (3i): M.p. 189-190 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 8.04 (s, 1H, NH), 7.87-7.19 (m, 12H, ArH), 7.01 (s, 1H, CH, indole ring), 4.97 (m, 1H, CH), 3.77-3.63 (m, 2H, CH₂). ¹³C NMR (100 MHz, DMSO-d₆): δ 37.4, 44.4, 111.2, 113.6, 117.9, 121.0, 123.7, 123.8, 126.2, 127.9, 128.4, 128.9, 130.1, 135.1, 135.5, 138.3, 144.9, 197.5. HRMS: m/z (%) cald. for C₂₃H₁₇NOClBr (M⁺) 437.0182, found 437.0180 (M⁺, 9.06).

3-(Benzod[1,3]dioxol-5-yl)-3-(5-bromo-1H-indol-3-yl)-1-phenylpropan-1-one (3j): M.p. 160-161 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 8.04 (s, 1H, NH), 7.93-6.80 (m, 10H, ArH), 6.75 (s, 1H, indole ring), 6.69-6.72 (m, 1H, ArH), 5.88 (m, 2H, CH₂) 4.91
A new synthetic method of Gallium dodecyl sulfate (Ga(DS)₃)

(t, 1H, J = 7.2 Hz, CH), 3.75-3.59 (m, 2H, CH₂). ¹³C NMR (100 MHz, DMSO-d₆): δ 37.1, 44.5, 100.78, 107.93, 108.36, 111.13, 113.51, 118.24, 120.81, 121.06 (2C), 123.6, 128.2, 128.4, 128.8, 133.3, 135.1, 137.0, 139.2, 145.4, 147.2, 198.4. HRMS: m/z (%) calcd. for C₂₄H₁₈NO₃Br (M⁺) 447.0470, found 447.0468(M⁺, 12.24).

4-Methyl-4-(7-methyl-1H-indol-3-yl)pentan-2-one (3k): M.p. 74-75 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.02 (s, 1H, NH), 7.67-6.99 (m, 3H, ArH), 6.92 (s, 1H, CH, indole ring), 2.96 (s, 2H, CH₂), 2.46 (s, 3H, CH₃), 1.72 (s, 3H, CH₃), 1.53 (s, 6H, 2×CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 17.9, 29.3, 32.3, 35.3, 55.9, 119.3, 120.2, 121.1, 121.2, 123.0, 124.8, 137.5, 209.6. HRMS: m/z (%) calcd. for C₁₅H₁₉NO (M⁺) 229.1467, found 229.1460 (M⁺, 25.07).

4-(7-Methyl-1H-indol-3-yl)butan-2-one (3l): M.p. 102-103 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.88 (s, 1H, NH), 7.46-6.90 (m, 4H, ArH), 2.94-2.91 (m, 2H, CH₂), 2.69-2.68 (m, 2H, CH₂), 2.22 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 17.1, 19.9, 30.6, 44.6, 116.0, 116.8, 119.9, 120.9, 121.6, 122.9, 127.0, 136.3, 209.5.

1-(4-Chlorophenyl)-3-(1-methyl-1H-indol-3-yl)-3-phenylpropan-1-one (3m): M.p. 142-143 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.85-6.99 (m, 13H, ArH), 6.81 (s, 1H, CH, indole ring), 5.03 (t, 1H, J = 7.2 Hz, CH), 3.79-3.66 (m, 5H, CH₂+CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 33.2, 38.6, 45.7, 109.7, 118.0, 119.4, 119.9, 122.2, 126.6, 126.8, 127.3, 128.2, 128.9, 129.3, 129.9, 135.8, 137.7, 139.9, 144.6, 199.8. HRMS: m/z (%) calcd. for C₂₄H₂₀ClNO (M⁺) 373.1233, found 373.1227 (M⁺, 31.89).

4-(2-Methyl-1H-indol-3-yl)butan-2-one (3n): oil. ¹H NMR (400 MHz, CDCl₃): δ 7.88 (s, 1H, NH), 7.44-7.06 (m, 4H, ArH), 6.99 (s, 1H, CH, indole ring), 3.07-3.03 (m, 2H, CH₂), 2.87-2.83 (m, 2H, CH₂), 2.48 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 11.5, 19.8, 41.5, 79.5, 111.4, 114.5, 118.9, 119.9, 121.6, 122.7, 126.1, 127.5, 127.4, 128.9, 136.5, 139.2, 208.5.

3,3’-(phenylmethylene)bis(1H-indole) (6a): m.p. 126-127 °C. ¹H NMR (400 MHz, CDCl₃): δ 5.88 (s, 1H, CH), 6.54-7.13 (m, 13H, ArH), 7.78 (s, 2H, 2NH). ¹³C NMR (100 MHz, CDCl₃): δ 40.6, 111.5, 119.6, 120.0, 120.3, 122.3, 124.1, 126.6, 127.4, 128.7, 129.1, 137.0, 144.4. HRMS (EI): calcd for C₂₃H₁₈N₂, 322.1470 [M⁺], found 322.1484.
3,3’-((2-nitrophenyl)methylene)bis(1H-indole) (6b): m.p. 137–140 °C. ^1H NMR (400 MHz, CDCl₃): δ 6.60 (s, 1H, CH), 6.64 (s, 2H, indole ring), 7.24–7.47 (m, 9H, ArH), 7.88–7.90 (m, 1H, ArH), 8.04 (s, 2H, 2NH). HRMS (EI): calcd for C_{23}H_{15}Br_{2}NO_{2}, 522.9531 [M⁺], found 522.9539.

3,3’-((4-chlorophenyl)methylene)bis(1H-indole) (6c): m.p. 89–91 °C. ^1H NMR (400 MHz, CDCl₃): δ 5.84 (s, 1H, CH), 6.59 (s, 2H, indole ring), 6.99–7.36 (m, 12H, ArH), 7.87 (s, 2H, 2NH). ^13C NMR (100 MHz, CDCl₃): δ 40.0, 111.5, 119.6, 119.8, 120.3, 122.5, 124.0, 127.3, 128.89, 130.5, 132.2, 137.1, 143.0.

4-(di(1H-indol-3-yl)methyl)phenol (6d): m.p. 76–78 °C. ^1H NMR (400 MHz, CDCl₃): δ 4.89 (brs, 1H, –OH), 5.78 (s, 1H, CH), 6.52–7.40 (m, 14H, ArH), 7.73 (s, 2H, 2NH). ^13C NMR (100 MHz, CDCl₃): δ 39.6, 108.4, 111.4, 115.3, 119.5, 120.1, 122.2, 123.9, 127.3, 136.9, 153.9.

3,3’-((3-nitrophenyl)methylene)bis(1H-indole) (6e): m.p. 85–87 °C. ^1H NMR (400 MHz, CDCl₃): δ 5.99 (s, 1H, CH), 6.63 (s, 2H, indole ring), 7.01–8.21 (m, 12H, ArH). ^13C NMR (100 MHz, CDCl₃): δ 39.6, 108.4, 111.5, 115.3, 119.5, 120.2, 120.3, 122.2, 124.0, 127.3, 130.1, 137.0, 154.01.

3,3’-((4-bromophenyl)methylene)bis(1H-indole) (6f): m.p. 112–113 °C. ^1H NMR (400 MHz, CDCl₃): δ 5.82 (s, 1H, CH), 6.56 (s, 2H, indole ring), 6.99–7.03 (m, 2H, ArH), 7.15–7.38 (m, 10H, ArH), 7.82 (s, 2H, 2NH). ^13C NMR (100 MHz, CDCl₃): δ 40.0, 111.6, 119.2, 119.7, 120.1, 120.3, 122.4, 124.1, 127.1, 130.8, 131.7, 136.9, 143.4. HRMS: (EI) calcd for C_{23}H_{15}Br_{2}N_{2}, 400.0575 [M⁺], found 400.0589.

3,3’-((4-chlorophenyl)methylene)bis(7-methyl-1H-indole) (6g): m.p. 156–158 °C. ^1H NMR (400 MHz, CDCl₃): δ 2.25 (s, 6H, 2CH₃), 5.66 (s, 1H, CH), 6.23 (s, 2H, indole ring), 7.07–6.80 (m, 10H, ArH), 7.34 (s, 2H, 2NH). ^13C NMR (100 MHz, CDCl₃): δ 16.9, 40.1, 118.0, 119.9, 120.0, 120.7, 123.0, 123.8, 126.8, 128.7, 130.4, 132.0, 136.6, 143.0.

3,3’-((4-chlorophenyl)methylene)bis(1-methyl-1H-indole) (6h): m.p. 185–187 °C. ^1H NMR (400 MHz, CDCl₃): δ 3.76 (s, 6H, 2CH₃), 6.00 (s, 1H, CH), 6.65 (s, 2H, indole ring), 7.13–7.16 (m, 2H, ArH), 7.32–7.52 (m, 10H, ArH). ^13C NMR (100 MHz, CDCl₃): δ 33.0, 39.9, 109.6, 118.1, 119.2, 120.3, 122.0, 127.7, 128.8, 130.5, 132.1, 137.8, 143.5.
A new synthetic method of Gallium dodecyl sulfate (Ga(DS)_3)

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