Synthesis and characterization Novel sulfonyl-containing fluorenes as materials for organic light-emitting diods

Assi. Prof. Salwa AbdulSattar Jabbar
College of Education for women
Chemistry Department, Tikrit University
Igor F. Perepichka **Sara abdulsattar Ahmed**
Chemistry Department, Bangor University, UK.

Abstract

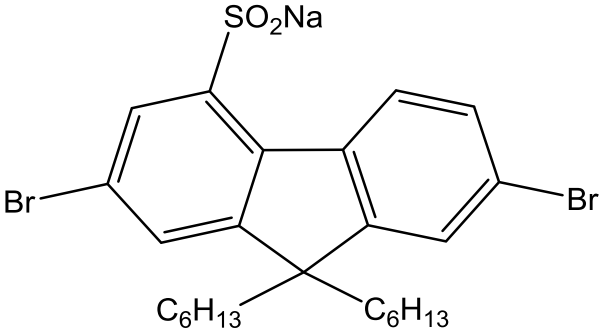
Fluorenes and their derivatives based on 2,7-disubstituted-9,9-dialkylfluorene as light-emitting diodes because of the high photoluminescent quantum efficiencies and thermal stabilities. The prepared compounds were characterized by FT-IR, H1NMR, C13NMR, MS, and UV/vis spectroscopy besides the melting points and C.H.N analysis. **Key words:** flourenes, and light emitting diods.

Introduction

It is well-known that substituted poly (2,7-fluorene) derivatives are attractive as active components of organic light-emitting diodes due to their thermal and chemical stability and their high emission quantum yields.[1-3] Small molecule organic light-emitting diodes are prepared by the consecutive vacuum-evaporation of several organic layers, where each layer fulfils a specific function such as charge injection, charge transport, or emission of light. By optimizing the properties of these layers, highly efficient small molecule organic light-emitting diodes have been prepared.[4] Light-emitting diodes electrophosphorescent at room temperature can be fabricated by processing the materials from solution. [5] The electrophosphorescont polymer based efficiency is limited by hole current and unbalanced in the polymer host as in poly light-emitting diodes polymer light-emitting diodes. [6,7] Their chemical synthesis, photophysics, and material properties are of interest not only as an academic curiosity but also as a commercial reality.[8,9]

Experimental:

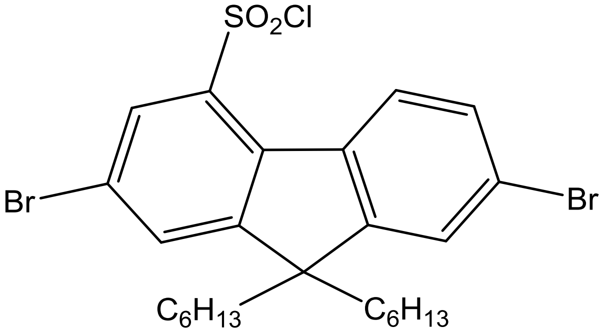
1: Synthesis of sodium 2,7-dibromo-9,9-dihexyl-fluorene-4-sulfinate (1).



(1)

2,7-Dibromo-9,9-dihexylfluorene (20.0 g, 74.1 mmol) and 600 mL of chloroform mixed. The solution was stirred for 15 minutes at room temperature and cool down to 0 °C. Chlorosulphonicacid (15.5 mL) was added slowly drop wise and stirred at 0 °C for 2 h. The reaction mixture was diluted with water (10 mL), white colour solid was precipitated. The solution was evaporated and dried in vacuo at room temperature to afford white colour solid (47.3 g, 203 %). The crude product was diluted with water stirred for 4 h (fully dissolution) then added NaOH solution (110 g in 400 mL of water) stirred for 10 h. White colour solid was precipitated filtered off and dried to afford white colour solid (30.7 g, 131%).

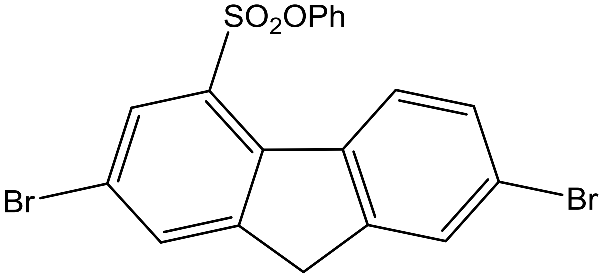
2: Synthesis of 2,7-dibromo-9,9-dihexyl-fluorene-4-sulfonyl chloride(2)



(2)

2,7-Dibromo-9,9-dihexylfluorene-4-sodiumsulfinate (29.6 g, 50.0 mmol), phosphourspenta chloride (13.0 g, 62.5 mmol), and 60 mL of phosphorousoxychloride was mixed. The reaction mixture was stirred at 120 °C (oil bath temperature) for 4 h. The reaction mixture was cooled to room temperature than evaporated $POCl_3$ solvent and dried in vacuo to give pale yellow crude product (52.9 g, 174.7 %). The crude product was purified by combi flash chromatography using petroleum ether as eluent to afford yellow colour oily compound (15.0 g, 73.8 %).

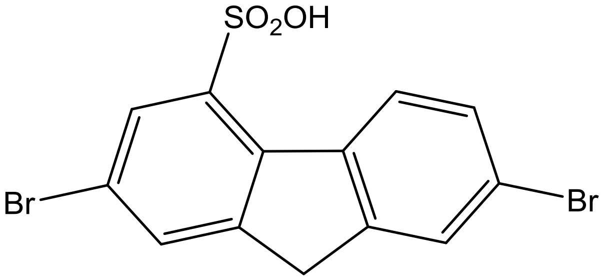
3: Synthesis of phenyl 2,7-dibromo-fluorene-4-sulfonate. (3)



(3)

2,7-Dibromo-4-sulfonylchloride (0.100 g, 0.236 mmol) and phenol (0.133 g, 1.419 mmol) was mixed. The reaction mixture was stirred at 100 °C for 30 minutes. The mixture was cooled to room temperature than added pyridine (1.5 mL) stirred at 100 °C for 2 h. The reaction mixture was diluted with water (3.5 mL) and extracted with dichloromethane (3×3.5 mL) the solution was evaporated and dried in vacuo to give orange colour liquid (0.103.g, 105 %). The crude product was purified by combi flash chromatography using Petroleum ether as eluent to afford yellow colour oily compound (17 mg, 17 %).

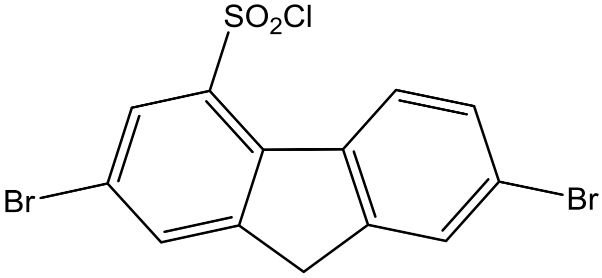
4: Synthesis of 2,7-dibromo-fluorene-4-sulfonic acid. (4)



(4)

2,7-Dibromofluorene (0.501 g, 1.54 mmol) and 13 mL of chloroform was mixed. The solution was stirred for 15 minutes at room temperature and cooled down to 0 °C, Chloro sulphonic acid (0.5 mL) was added slowly drop wise and stirred at 0 °C for 2 h. Filtered off the solid and dried on freeze dryer. White colour solid (1.02 g, 163%). Tried to recrystallized crude product with 1,4-dioxane and it's dissolved in 2 mL from 1,4-dioxan with reflux 1h and added 10 mL hexane and cooling to room temperature. Next day filtered off the solid, washed with hexane 2 ml and dried on freeze dryer. Cream colour solid (0.71 g, 114%).

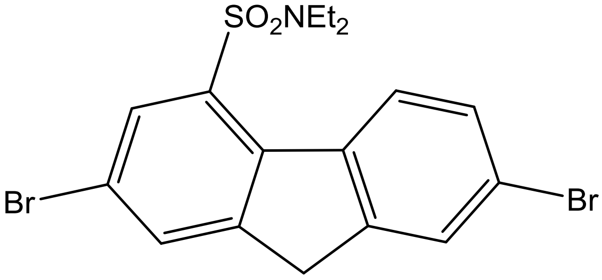
5: Synthesis of 2,7-dibromo-fluorene-4-sulfonyl chloride. (5)



(5)

2,7-Dibromofluorene-4-sulphonicacid (0.500 g, 1.236 mmol) phosphourspenta chloride (0.322 g, 1.540 mmol), and (2.06 g, 7.53 mmol) of phosphorousoxy chloride was mixed. The reaction mixture was stirred at 120 °C for 4 h. The reaction mixture was evaporated to remove $POCl_3$ solvent and dried in vacuo to give brown crude product (0.42 g, 80 %). The crude product was purified by combi flash chromatography using petroleum ether / dichloromethane 1:1 as eluent to afford yellow colour oily compound (96 mg, 18.4 %).

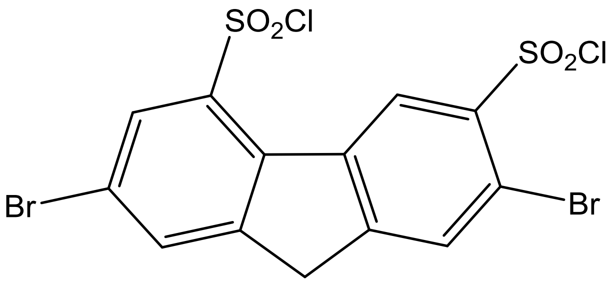
6: Synthesis of 2,7-dibromo-N,N-diethyl-fluorene-4-sulfonamide. (6)



(6)

2,7-Dibromofluorene-4-sulfonylchloride (0.100 g, 0.236 mmol) and 8 mL of THF was mixed. To this solution diethylamine 0.082 gm added drop wise left stirred at room temperature for 3 h and after 3 h added 50 mL water to the solution. The precipitate was filtered off, washed with water (3×1.0 mL) and dried on freeze dryer. Yellow solid (0.04 g, 40.7 %).

7: Synthesis of 2,7-dibromo-fluorene-4,6-disulfonyl dichloride. (7)



(7)

2,7-Dibromofluorene (0.501 g, 1.546 mmol) was mixed. Chlorosulphonicacid (4.0 mL, 60 mmol) was added slowly and reaction mixture was stirring for 2 h at room temperature. After 15 min green colour with precipitate, washed the mixture with 5 mL water, and the solid was filtered off, dried on freeze dryer. White colour solid (0.64 g, 79.2 %).

Table (1) some physical properties for compounds (1-14)

No.of comp	M.W	m.p ° C	Solvent of purify	Yield %	Colour
1	572.4	255 dec	___	131	White
2	590.8	94-96	PE	174	Yellow
3	478.5	168-170	PE	105	Orange
4	627.6	108-110	PE/DCM 1:1	85	Yellow
5	648.5	135-137	PE/DCM 2:1	84	White
6	689.6	159-161	PE/DCM 4:1	15	White
7	404	237 dec	___	114	Off white

PE = Petroleum ether
DCM = Dichloromethane

Results and Dissection

Characterization of compound (1)

The ^{1}H NMR (for $Br_2(C_6H_{13})_2SO_3HFl$ 400 MHz, $CDCl_3$): δ (ppm) 8.65 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 1.7 Hz, 1H), 7.90 (d, J = 1.6 Hz, 1H), 7.70 (d, J = 1.8 Hz, 1H), 7.56 (dd, J = 8.4, 1.9 Hz, 1H), 2.15 (t, J = 8.2 Hz, 4H, $CH_2C_5H_{11}$), 1.14-1.00 (m, 12H, $CH_2C_3H_6CH_2CH_3$), 0.76 (t, J = 6.8 Hz, 6H, $C_5H_{11}CH_3$), 0.62-0.52 (m, 4H, $C_4H_8CH_2CH_3$).

Also ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ (ppm) 155.11, 153.16, 136.48, 136.40, 135.95, 130.58, 129.60, 128.94, 127.30, 125.50, 122.90, 120.52, 54.87, 40.33, 31.36, 29.48, 23.49, 22.55, 13.94.

MS (TOF EI$^+$): *m/z* 572.00 (M$^+$, ^{79}Br, ^{79}Br), 573.92 (M$^+$, ^{79}Br/^{81}Br), 573.00 (M$^+$, ^{81}Br/^{81}Br).

Calcd for $C_{25}H_{32}Br_2O_3S$: m/z: 572.04 (100.0%), 574.04 (52.2%), 573.05 (27.2%).

Characterization of compound (2)

The ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.41 (d, J = 8.6 Hz, 1H), 8.20 (d, J = 1.6 Hz, 1H), 7.76 (d, J = 1.6 Hz, 1H), 7.58 (dd, J = 8.6, 1.8 Hz, 1H), 7.51 (d, J = 1.7 Hz, 1H), 1.97 (t, J = 8.6 Hz, 4H, $CH_2C_5H_{11}$), 1.14-1.03 (m, 12H, $CH_2C_3H_6CH_2CH_3$), 0.78 (t, J = 7.0 Hz, 6H, $C_5H_{10}CH_3$), 0.62-0.44 (m, 4H, $C_4H_8CH_2CH_3$).

^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 156.67, 153.73, 139.15, 136.60, 134.77, 132.25, 131.11, 130.31, 128.66, 125.91, 124.57, 120.55, 55.50, 53.42, 40.22, 31.32, 29.37, 23.44, 22.51, 13.94.

MS (TOF EI$^+$): *m/z* 589.87 (M$^+$, ^{79}Br, ^{79}Br), 591.87 (M$^+$, ^{79}Br/^{81}Br), 587.82 (M$^+$, ^{81}Br/^{81}Br).

Calcd for $C_{25}H_{31}Br_2ClO_2S$: m/z: 590.01 (100.0%), 592.01 (51.4%), 588.01 (48.6%).

Characterization of compound (3)

The ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.66 (d, *J* = 8.6 Hz, 1H), 8.11 (d, *J* = 1.2 Hz, 1H), 8.01 (s, 1H), 7.82 (s, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 4.08 (s, 2H).

^{13}C NMR (14SAA-011) (100 MHz, (CD$_3$)$_2$CO): δ (ppm) 147.39, 146.37, 143.97, 138.74, 136.01, 129.74, 129.43, 128.82, 128.71, 127.37, 120.78, 119.30, 36.67.

MS (TOF EI$^+$): *m/z* 403.90 (M$^+$, ^{79}Br, ^{79}Br), 402.00 (M$^+$, ^{79}Br/^{81}Br), 405.85 (M$^+$, ^{81}Br/^{81}Br).

Calcd for $C_{13}H_8Br_2O_3S$ m/z : 403.85 (100.0%), 401.86 (51.4%), 405.85 (48.6%).

Characterization of compound (4)

The ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.66 (d, *J* = 8.6 Hz, 1H), 8.11 (d, *J* = 1.2 Hz, 1H), 8.01 (s, 1H), 7.82 (s, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 4.08 (s, 2H).

^{13}C NMR (14SAA-011) (100 MHz, (CD$_3$)$_2$CO): δ (ppm) 147.39, 146.37, 143.97, 138.74, 136.01, 129.74, 129.43, 128.82, 128.71, 127.37, 120.78, 119.30, 36.67.

MS (TOF EI$^+$): *m/z* 403.90 (M$^+$, ^{79}Br, ^{79}Br), 402.00 (M$^+$, ^{79}Br/^{81}Br), 405.85 (M$^+$, ^{81}Br/^{81}Br).

Calcd for $C_{13}H_8Br_2O_3S$ m/z : 403.85 (100.0%), 401.86 (51.4%), 405.85 (48.6%).

Characterization of compound (5)

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.49 (d, *J* = 8.6 Hz, 1H), 8.27 (d, *J* = 1.2 Hz, 1H), 8.00 (d, *J* = 0.8 Hz, 1H), 7.77 (d, *J* = 084 Hz, 1H), 7.65 (dd, *J* = 8.6, 1.7 Hz, 1H), 4.02 (s, 1H).

^{13}C NMR (100 MHz, CDCl$_3$): 148.50, 145.99, 139.17, 137.15, 135.49, 134.62, 131.12, 130.34, 128.64, 128.12, 123.95, 120.02, 36.90.

MS (TOF EI$^+$): *m/z* 421.80 (M$^+$, ^{79}Br, ^{79}Br), 423.81 (M$^+$, ^{79}Br/^{81}Br), 419.80 (M$^+$, ^{81}Br/^{81}Br).

Calcd for $C_{13}H_7Br_2ClO_2S$: 421.82 (100.0%), 423.82 (72.8%), 419.82 (43.3%).

Characterization of compound (6)

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.49 (d, *J* = 8.6 Hz, 1H), 7.84 (s, 1H), 7.83 (s, 1H), 7.68 (s, 1H), 7.55 (dd, *J* = 8.6, 1.8 Hz, 1H), 3.92 (s, 1H), 3.42 (q, *J* = 7.1 Hz, 4H, N-CH_2CH$_3$), 1.22 (t, *J* = 7.1 Hz, 6H, N-CH$_2$$CH_3$).

<u>^{13}C NMR</u> (100 MHz, CDCl$_3$): δ (ppm) 148.13, 145.49, 137.33, 136.87, 135.58, 131.78, 130.46, 129.40, 127.77, 127.68, 122.67, 119.85, 53.42, 42.03, 36.71, 30.92, 14.06.

<u>MS</u> (TOF EI$^+$): *m/z* 458.85 (M$^+$, ^{79}Br, ^{79}Br), 460.84 (M$^+$, ^{79}Br/^{81}Br), 456.84 (M$^+$, ^{81}Br/^{81}Br).

Calcd for $C_{17}H_{17}Br_2NO_2S$ m/z: 458.93 (100.0%), 460.93 (52.0%), 456.93 (50.2%)

Characterization of compound (7)

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 9.49 (s, 1H), 8.33 (d, *J* = 1.6 Hz, 1H), 8.11 (s, 1H), 8.09 (s, 1H), 4.15 (s, 2H). Purity of the compound 80 %.

<u>^{13}C NMR</u> (100 MHz, CDCl$_3$): δ (ppm) 151.36, 148.17, 142.87, 139.82, 136.68, 134.99, 134.91, 132.59, 131.03, 129.23, 122.17, 121.18, 37.13

<u>MS</u> (TOF EI$^+$): *m/z* 519.82 (M$^+$, ^{79}Br, ^{79}Br), 521.82 (M$^+$, ^{79}Br/^{81}Br), 521.99 (M$^+$, ^{81}Br/^{81}Br).

Calcd for $C_{13}H_6Br_2Cl_2O_4S_2$ m/z: 519.74 (100.0%), 521.74 (63.9%), 517.75 (51.4%).

References

1- Wong, K. T.; Chien, Y. Y.; Chen, R. T.; Wang, C. F.; Lin, Y. T.; Chiang, H. H.; Hsieh, P. Y.; Wu, C. C.; Chou, C. H.; Su, Y. O. *J. Am. Chem. Soc.*, *124*, 11576, **2002.**

2- Yu, W. L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater.12*, 828, **2000**.

3- Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc. 123*, 946, **2001**.

4- Addy van Dijken, Jolanda J. A. M. Bastiaansen, Nicole M. M. Kiggen, Bea M. W. Langeveld, Carsten Rothe, Andy Monkman, Ingrid Bach,| Philipp Sto¨ ssel,| and Klemens Brunner. J. AM. CHEM. SOC. 126, 7718-7727, **2004.**

5- M. D. McGehee, T.Bergste dt, C. Zhang, A. P. Saab, M. B. O'Regan, G. C. Bazan, V. I. Srdanov, A. J. Heeger, Adv. Mater. 11, 1349, **1999**.

6- D. V. Kharamtchenkov, V. I. Arkhipov, H. BASSLER, J. Appl. Phys. 81, 6954, **1997**.

7- Y. Cao, G. M. Treacy, P. Smith, A. J. Hegger, Appl. Phys. Lett. 60, 2711, **1992**.

8- (a) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2586. (b) Nguyen, P.; Go´mez-Elipe, P.; Manners, I. *Chem. Re*V. **1999**, *99*, 1515.
(c) Manners, I. *Synthetic Metal-Containing Polymers*; Wiley-VCH: Weinheim, 2004. (d) Szafert, S.; Gladysz, J. A. *Chem. Re*V.**2003**, *103*, 4175.
(e) Silverman, E. E.; Cardolaccia, T.; Zhao, X.; Kim, K. Y.; Haskins-Glusac, K.; Schanze, K. S. *Coord. Chem. Re*V. **2005**, *249*, 1491.
(f) Wong, W.-Y. *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 197.
(g) Wong, W.-Y. *Comment Inorg. Chem. 26*, 39, **2005.**
9- (a) Wilson, S.; Dhoot, A. S.; Seeley, A. J. A. B.; Khan, M. S.; Ko¨hler, A.; Friend, R. H. *Nature* **2001**, *413*, 828.
(b) Chawdhury, N.; Ko¨hler, A.; Friend, R. H.; Wong, W.-Y.; Lewis, J.; Younus, M.; Raithby, P. R.; Corcoran, T. C.; Al-Mandhary, M. R. A.; Khan, M. S. *J. Chem. Phys. 110*, 496, **1999.**