

Supplementary Material

Synthesis, optical and electrochemical properties of new thieno[2,3-*b*]indole-based dyes

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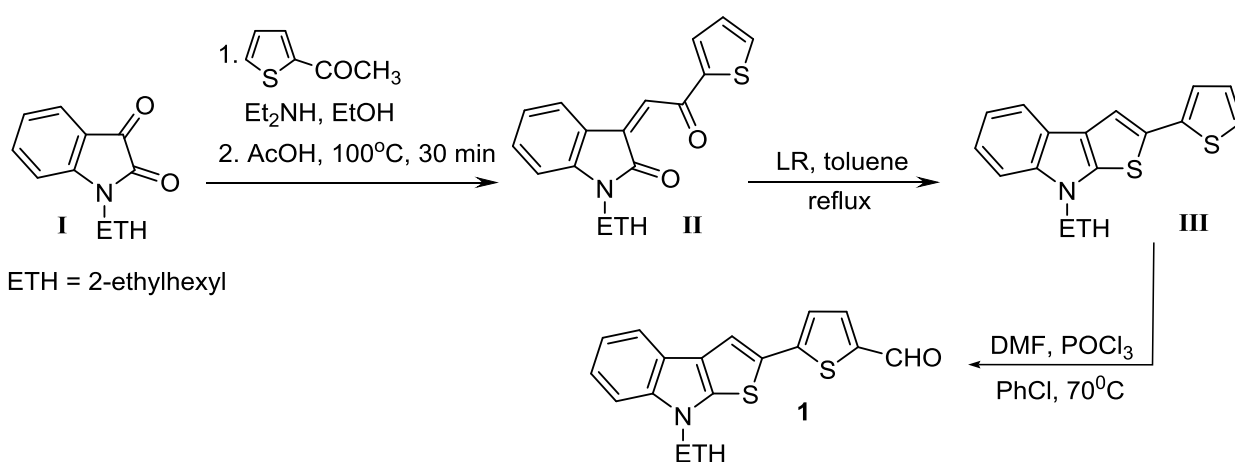
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[1] Synthesis of the starting 5-{8-(2-ethylhexyl)-8H-thieno[2,3-b]indole-2-yl}thiophene-2-carbaldehyde (**1**)

Chalcone (**II**), 8-(2-ethylhexyl)-2-(thiophen-2-yl)-8H-thieno[2,3-b]indole (**III**) and 5-{8-(2-ethylhexyl)-8H-thieno[2,3-b]indole-2-yl}thiophene-2-carbaldehyde (**I**) were prepared according to the same procedures, which had been described in the recently published paper [11] and used for the synthesis of the chalcone series, including N-alkyl-3-substituted indolin-2-one moieties, 5-aryl(heteryl)thieno[2,3-b]indoles and their aldehydes (Scheme 1S).



Scheme 1S. Synthetic protocol of 5-{8-(2-ethylhexyl)-8H-thieno[2,3-b]indole-2-yl}thiophene-2-carbaldehyde (**1**) preparation.

a) Synthesis of 1-(2-ethylhexyl)-3-(2-oxo-2-(thiophen-2-yl)ethylidene)indolin-2-one (**II**)

Solution of 1-(2-ethylhexyl)isatin (**I**) (0.77 g, 3 mmol), acetylthiophene (0.38 g, 3 mmol) and *N,N*-diethylamine (0.062 mL, 0.6 mmol) in EtOH (15 mL) was stirred at room temperature for 48 h. The resulting mixture was concentrated under reduced pressure to obtain crude adduct that was then dehydrated without any purification, for what purpose a drop of hydrochloric acid was added to the suspension of a crude adduct in acetic acid (3 mL). The resulted mixture was stirred at 100 °C for 30 min and afterwards cooled to form a precipitate, which was filtered off, washed with methanol and dried in the air to give indolin-2-one as thick red oil, yield 59%. Thus prepared chalcone **I** was used further without additional purification. ¹H NMR (CDCl₃, 300 MHz) δ: 0.87 (t, 3H, *J* 8.3 Hz), 0.92 (t, 3H, *J* 8.3 Hz), 1.35 (m, 8H), 2.11 (m, 1H), 4.06 (d, 2H, *J* 8.6 Hz), 7.12 (t, 1H, *J* 4.3 Hz), 7.02 (t, 1H, *J* 8.3 Hz), 7.12 (t, 1H, *J* 4.3), 7.17 (d, 1H, *J* 7.6 Hz), 7.34 (d, 1H, *J* 7.6 Hz), 7.36 (t, 1H, *J* 9 Hz), 7.46 (s, 1H), 7.74 (d, 1H, *J* 5.3 Hz), 7.93 (d, 1H, *J* 4.6 Hz). Mass spectrum, *m/z* (*I*_{rel}, %): 367.1 [*M*]⁺ (100), 368.1 [*M*+1H]⁺ (25.8), 369.05 [*M*+2H]⁺ (11.4), 270 (9.6), 269 (41.7), 268 (49.1), 256 (19.0), 255 (19.0), 158 (18.6), 130 (10.1), 129 (13.6), 111 (100), 97 (11.4).

b) Synthesis of 8-(2-ethylhexyl)-2-(thiophen-2-yl)-8H-thieno[2,3-b]indole (**III**)

Lawesson's reagent (0.40 mg, 1 mmol) was added to the solution of 0.17 g (1 mmol) 1-(2-ethylhexyl)-3-(2-oxo-2-(thiophen-2-yl)ethylidene)indolin-2-one (**II**) in dry toluene (5 mL), the

resulting mixture was refluxed for 1 h, then concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 and filtered through a silica gel pad. Evaporation of CH_2Cl_2 gave rise to a crude product, which was purified by column chromatography giving thieno[2,3-*b*]indole **III** as red-orange thick oil, yield 59%.

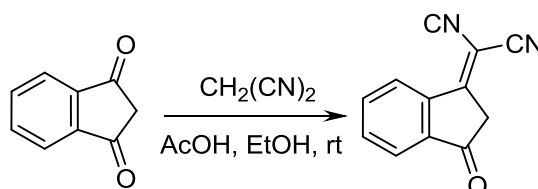
^1H NMR (CDCl_3 , 300 MHz) δ : 0.84 (t, 3H, J 7.3 Hz), 0.91 (t, 3H, J 8.6 Hz), 1.35 (m, 8H), 2.11 (m, 1H), 4.04 (d, 2H, J 8.6 Hz), 7.00 (t, 1H, J 5.0 Hz), 7.06 (d, 1H, J 4.6), 7.13 (d, 1H, J 4.0 Hz), 7.16 (t, 1H, J 7.3 Hz), 7.25 (t, 1H, J 7.6 Hz), 7.34 (d, 1H, J 9.0 Hz), 7.46 (s, 1H), 7.77 (d, 1H, J 7.6 Hz). Mass spectrum, m/z (I_{rel} , %): 367.1 $[\text{M}]^+$ (100), 368.1 $[\text{M}+1\text{H}]^+$ (2), 368.2 (24), 369.1 (9), 369.2 (3), 370.1 (2).

c) Formylation of 8-(2-ethylhexyl)-2-(thiophen-2-yl)-8*H*-thieno[2,3-*b*]indole (**III**).

POCl_3 (0.28 ml, 3 mmol) was added to DMF solution (0.37 ml, 3 mmol) in dry PhCl. The solution was stirred at rt for 30 min; afterwards 8-(2-ethylhexyl)-2-(thiophen-2-yl)-8*H*-thieno[2,3-*b*]indole (**III**) (0.36 g, 1 mmol) was admixed. The resulting reaction mixture then heated at 50–60°C for 6 hours. The whole reaction mixture was poured into ice-water (50 ml) and extracted the organic layer using dichlorometane (3 \times 30 ml). The solvent was dried under reduced pressure and the crude product was subjected to silica gel column chromatography to give the carbaldehyde **1** as a yellow powder; yield 79%. ^1H NMR (CDCl_3 , 300 MHz) ppm: 0.87 (t, 3H, J 8.3 Hz), 0.92 (t, 3H, J 8.3 Hz), 1.35 (m, 8H), 2.01 (m, 1H), 4.05 (d, 2H, J 8.0 Hz), 7.17 (d, 1H, J 4.6 Hz), 7.20 (t, 1H, J 9.0 Hz), 7.29 (t, 1H, J 8.3 Hz), 7.35 (d, 1H, J 8.6 Hz), 7.64 (d, 1H, J 4.3 Hz), 7.67 (s, 1H), 7.95 (d, 2H, J = 8.3 Hz), 9.81 (s, 1H, CHO). Mass spectrum, m/z (I_{rel} , %): 395.95 $[\text{M}]^+$ (100), 396.2 $[\text{M}+1\text{H}]^+$ (27.9), 397.2 $[\text{M}+2\text{H}]^+$ (12.9), 297 (13), 296 (63.3), 283 (20).

[2] Synthesis of 2-(3-oxo-2,3-dihydroindene-1-ylidene)malononitrile.

2-(3-Oxo-2,3-dihydroindene-1-ylidene)malononitrile was prepared according the synthetic procedure described by K.A. Bello *et al.* ²⁴.



Scheme 2S. Synthesis of 2-(3-oxo-2,3-dihydroindene-1-ylidene)malononitrile.

Anhydrous sodium acetate (1.6 g, 19.5 mmol) was added at rt to the stirred mixture of indane-1,3-dione (2.19 g, 14.98 mmol), malononitrile (1.98 g, 30 mmol) in 25 ml of absolute ethanol. An immediate red coloration occurred and the suspended solid slowly dissolved. After 40 min the mixture was diluted with water (50 ml) and acidified to pH 1–2 by addition of conc. hydrochloric acid. The suspension was additionally stirred for 10 min; the resulting solid material was then filtered off and washed thoroughly with water. The crude product was recrystallized twice from acetic acid to give the target product (~ 90%), m.p. 230–231°C (223–229°C Lit. ²⁵).

[3] Equations for the determination of the empirical HOMO- LUMO energy levels.

The empirical HOMO energy levels ($E_{\text{HOMO, cv}}$) of the dyes **2-4** were obtained using Equation (1)¹⁵:

$$E_{\text{HOMO}} = - (E_{\text{ox}}^{\text{onset}} \text{ vs Ag/AgCl} - E_{\text{Fc}} \text{ vs Ag/AgCl} + 4.8) \text{ eV} \quad (1)$$

where $E_{\text{Fc}} \text{ vs Ag/AgCl} = +0.41 \text{ V}$.

The LUMO energy levels ($E_{\text{LUMO, cv}}$) of dyes **2-4** were calculated based on $E_{\text{HOMO, cv}}$ and optical band gap by Equation (2)¹⁵:

$$E_{\text{LUMO, cv}} = (E_{\text{HOMO, cv}} + E_{\text{g}}^{\text{opt}}) \text{ eV} \quad (2)$$