

# A facile synthesis of linear benzene-fused bis(tetrathiafulvalene) compounds and their application for organic field-effect transistors†

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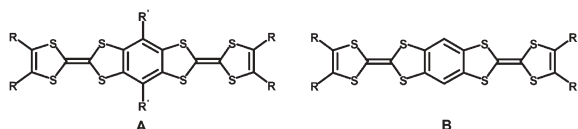
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Three new linear benzene-fused bis(tetrathiafulvalene) compounds (1–3) were easily synthesized by one-step phosphite-induced cross-coupling reactions; a solution processed organic field-effect transistor based on 2 shows high mobility of 0.02 cm<sup>2</sup>/Vs.

Tetrathiafulvalene (TTF) and its derivatives have been intensively investigated in the field of organic conductors and superconductors.<sup>1</sup> In recent years, molecular devices based on TTF derivatives, such as molecular switches,<sup>2</sup> sensors,<sup>3</sup> self-assembled redox-active supermolecules<sup>4</sup> and field-effect transistors (OFETs),<sup>5</sup> have attracted more and more attention, because of their novel properties and potential applications. Dimeric TTFs (A, Scheme 1, R' = alkyloxy, thioalkyl substituents or F)<sup>6</sup> linked by a central substituted benzene core have been synthesized by Müllen and co-workers<sup>7</sup> and by Moradpour *et al.*,<sup>8</sup> using long difficult synthetic paths. As organic conducting materials, charge transfer (CT) complexes and radical-cation salts of these benzene-fused bis-TTFs were studied<sup>7</sup> and some of their cation radicals, as the mixed valence organic species, were investigated for intervalence transition.<sup>8</sup>

Benzene-fused bis-TTFs have new structural and electrochemical features with respect to mono-TTFs; the expanded  $\pi$ -conjugation with two interacting TTF units leads to more oxidized cation radicals (bis-TTF<sup>+</sup>, bis-TTF<sup>2+</sup>, bis-TTF<sup>3+</sup> and bis-TTF<sup>4+</sup>) and multi-step redox behavior.<sup>6–9</sup> Considering these characteristics, benzene-fused bis-TTFs should be endowed with new opportunities to act as good candidate molecules for redox-switches, sensors and OFETs. However, the ideal benzene-fused bis-TTFs without central substituents (B, Scheme 1), which can form more efficient intermolecular  $\pi$ - $\pi$  stacks than type A compounds,<sup>7,9</sup> have not been synthesized in the past owing to the very low solubility of the precursor 1,3,5,7-tetrathia-s-indacene-2,6-dithione (4)<sup>10</sup> (Scheme 2) in organic solvents.<sup>7</sup> In this communication, we



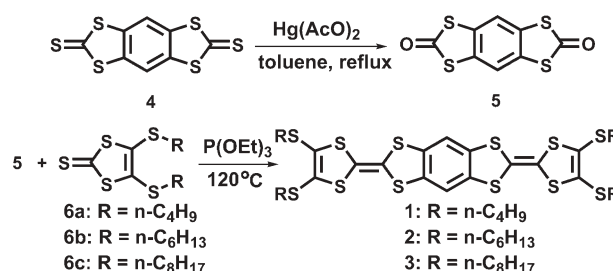
Scheme 1

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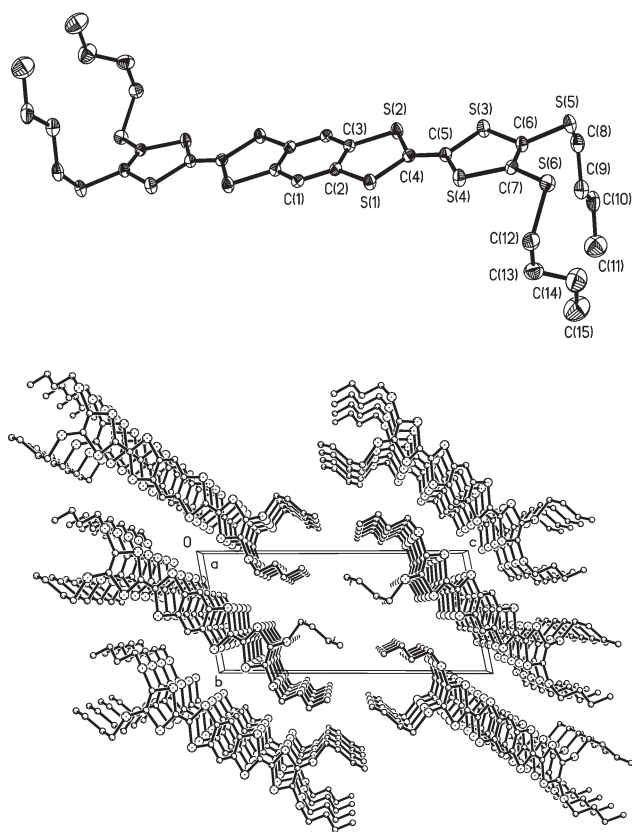


Scheme 2

present a one-step synthesis of type B compounds (1–3) using 1,3,5,7-tetrathia-s-indacene-2,6-dione (5)<sup>11</sup> as the precursor (Scheme 2) and the solution spin-coating field-effect transistors based on 1–3 are also studied.

The virtual insolubility of 4 obstructs its further use as a precursor for the synthesis of type B benzene-fused bis-TTFs. With this in mind, we tried to obtain 5, which is soluble in common organic solvents and has higher activity for phosphite-induced cross-coupling reactions. As shown in Scheme 2, 5 was readily synthesized in 87% yield by reacting 4 (which can be easily prepared<sup>10</sup>) with 4 equiv. of Hg(AcO)<sub>2</sub> in refluxing toluene for 12 h, instead of by the reported synthesis<sup>11</sup> which involves handling highly toxic phosgene. The phosphite-induced cross-coupling reactions of 5 with excess of 6 (a, b or c)<sup>12</sup> in P(EtO)<sub>3</sub> at 120 °C for 24 h (Scheme 2) afforded 1–3 in 38%, 52% and 38.5% yield, respectively. 1–3 were easily purified by re-crystallization and characterized by elemental analysis, MS (EI, MALDI-TOF), <sup>1</sup>H-NMR, and FT-IR (see ESI†). ‡ 1–3 are moderately soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, THF and 1,2-dichlorobenzene with the order of solubility of 2 > 1 > 3.

Fig. 1 shows the molecular and crystallographic packing structures of 1. § The molecule lies about an inversion center. The entire  $\pi$ -system is planar; the mean atom deviation from the plane based on the C<sub>14</sub>S<sub>12</sub> skeleton is 0.03 Å. Four terminal butyl chains are turned almost perpendicularly out of the planar  $\pi$ -system, affording a chair-like molecular conformation. Molecules of 1 form a columnar stacking along the crystallographic *a*-axis direction with an interplanar separation of 3.48 Å. The adjacent molecules are shifted about half a TTF subunit from each other, affording a nearly 4/5 intermolecular  $\pi$ -overlap, which is much larger than for the stacking type A molecules (R = S-hexyl and R' = O-hexyl) reported by Müllen *et al.*<sup>9b</sup> The results might indicate that type B compounds can form more efficient intermolecular  $\pi$ - $\pi$  interactions than type A compounds, because a close stacking of type A molecules is prevented by central O- or S-alkyl substituents.<sup>7,9</sup>



**Fig. 1** Molecular structure (top) and stacking structure (bottom) of **1**, in which the H atoms are omitted for clarity.

The solution electrochemical properties of **1–3** were investigated by cyclic voltammetry (CV). The results are summarized in Table 1. Similar to type A compounds,<sup>7,8</sup> **1–3** exhibit four sequential quasi-reversible one-electron transfer steps, ultimately yielding the fully oxidized tetravalent cation. Their HOMO levels obtained from the CV data are about  $-4.9$  eV. The results (see Table 2) of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) indicate that **1–3** have good thermal stability, after melting; the onset decomposition occurred at about  $300$  °C. The longer alkyl chains resulted in a lower melting point ( $T_m$ , from

**Table 1** Half-wave potentials of **1–3** vs. Ag/AgCl in  $\text{CH}_2\text{Cl}_2$  with  $0.1$  M  $n\text{-Bu}_4\text{NPF}_6$  as supporting electrolyte (scan speed =  $50$  mV/s)

Compound	$E^1_{1/2}$ (V)	$E^2_{1/2}$ (V)	$E^3_{1/2}$ (V)	$E^4_{1/2}$ (V)	HOMO <sup>a</sup> (eV)
<b>1</b>	0.52	0.71	1.07	1.20	$-4.87$
<b>2</b>	0.52	0.72	1.07	1.19	$-4.86$
<b>3</b> <sup>b</sup>	0.56	0.80	1.09	1.24	$-4.91$

<sup>a</sup> Calculated based on  $\text{HOMO} = -(E_{\text{ox}}^{\text{onset}} + 4.4)$  eV. <sup>b</sup> Measured in  $\text{CHCl}_3$  due to the poor solubility of **3** in  $\text{CH}_2\text{Cl}_2$ .

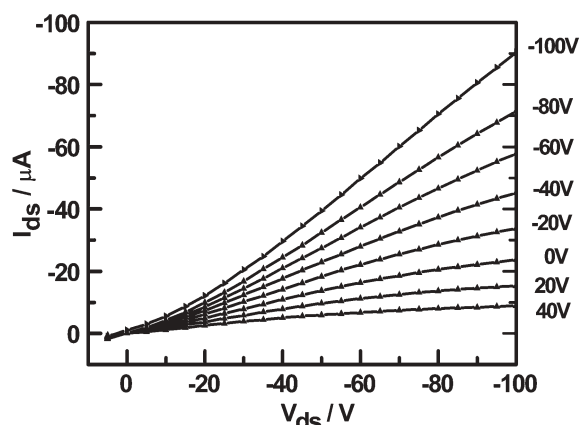
**Table 2** Physical properties of **1–3**

Compound	$T_m$ (°C)	$T_d$ (°C)	Band gap (eV)	Mobility ( $\text{cm}^2/\text{Vs}$ )	$I_{\text{on}}/I_{\text{off}}$
<b>1</b>	201	296	2.88	$5 \times 10^{-3}$	$10^2$
<b>2</b>	174	299	2.87	$2 \times 10^{-2}$	$10^2$
<b>3</b>	163	301	2.86	$6.7 \times 10^{-5}$	$10^3$

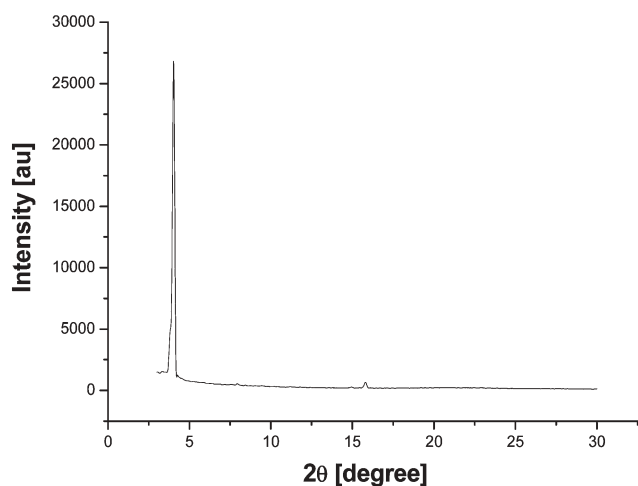
$201$  to  $163$  °C), but the onset decomposition temperature ( $T_d$ ), from  $296$  to  $301$  °C, was slightly enhanced. The HOMO–LUMO gaps of **1–3** are near to  $2.9$  eV (Table 2), estimated from the absorption edges in  $\text{CH}_2\text{Cl}_2$ , indicating good redox stability.<sup>13</sup>

As compared with most mono-TTFs<sup>5f</sup> used for OFETs, **1–3** have more extended  $\pi$ -conjugation, which can increase intermolecular  $\pi$ – $\pi$  interactions. On the other hand, they bear four terminal alkyl chains (carbon atoms, 4, 6 or 8), which not only ensure the solubility of the molecules but also facilitate the stacking of central  $\text{C}_{14}\text{S}_{12}$  skeletons by van der Waals interactions of the alkyl chains.<sup>14</sup> These structural characteristics of **1–3** are expected to improve the mobilities of their FET devices. Thin films ( $30$ – $50$  nm) of **1–3** were deposited on  $\text{SiO}_2/\text{Si}$  substrates by spin-coating the solutions (**1**, **2** in  $\text{CHCl}_3$  and **3** in 1,2-dichlorobenzene for its lower solubility in  $\text{CHCl}_3$ ,  $0.6$ – $0.8$  wt%). An n-type Si wafer with a  $\text{SiO}_2$  layer of  $450$  nm and a capacitance of  $10$  nF  $\text{cm}^{-2}$  was used as the gate; gold source and drain contacts ( $50$  nm) were deposited on the organic layer through a shadow mask, affording a bottom-gate configuration. The channel length ( $L$ ) and width ( $W$ ) were  $50$   $\mu\text{m}$  and  $3$  mm, respectively. The FET measurements were carried out at room temperature in air using a semiconductor parameter analyzer. To our knowledge, these devices are the first examples of solution processed thin film OFETs based on TTFs and of oligomeric TTF-based OFETs.

The FET characteristics are summarized in Table 2. Fig. 2 shows the output characteristics of the device based on **2**. All three devices showed p-type behavior and the field-effect mobilities were estimated from the linear regime.<sup>15</sup> The device based on **2** (Scheme 2,  $R = n\text{-C}_6\text{H}_{13}$ ) afforded the highest mobility of  $0.02$   $\text{cm}^2/\text{Vs}$ , which is quite high among the solution processed thin film FET devices based on small organic molecules.<sup>16</sup> The dependence of field-effect mobility on alkyl chain length was also found for poly(3-alkylthiophene)-based FET devices, in which the poly(3-hexylthiophene)-based devices showed the highest mobilities.<sup>17</sup> The threshold voltage of these devices is relatively high ( $39$ ,  $54$  and  $17$  V for **1–3**, respectively), indicating the existence of rich carriers in the active layer under zero gate voltage, which might be one of the main reasons for the low on/off current ratios. To improve the FET performance, optimization of fabrication techniques and synthesis of new benzene-fused bis-TTF compounds with higher function are now in progress.



**Fig. 2** Drain current versus drain voltage as a function of gate voltage for FETs based on **2** at room temperature.



**Fig. 3** X-ray diffraction of a spin-coated thin film of **2** on SiO<sub>2</sub>/Si substrate at room temperature.

The thin films of **1–3** deposited on SiO<sub>2</sub>/Si substrates by solution spin-coating were investigated by X-ray diffraction (XRD) in reflection mode. Fig. 3 shows the thin film XRD patterns of **2** at room temperature. Sharp reflections up to the second or higher order were observed in all three films, indicating the formation of lamellar ordering and crystallinity on the substrate. The d-spacings obtained from the first reflection peaks (1.77, 2.20 and 2.79 nm, respectively) are shorter than the extended molecular lengths optimized by ChemDraw 3D and calculated by Material Studio 3.0 (2.87, 3.38 and 3.86 nm, respectively), implying the declining orientation of the molecules of **1–3** on the substrate.

In conclusion, we present a facile synthesis of linear benzene-fused bis-TTF compounds without substituents on the benzene core. The synthesis utilizes a phosphite-induced cross-coupling reaction to couple two easily prepared synthons, 1,3,5,7-tetrathia-s-indacene-2,6-dione (**5**) and the corresponding 1,3-dithiole-2-thione. Our studies also show that type B benzene-fused bis-TTF compounds can act as good candidates for OFETs.

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## Notes and references

‡ <sup>13</sup>C-NMR spectra of **1–3** (in CDCl<sub>3</sub>) cannot give enough signals even when measured at 50 °C for 10 hours. Because of the strong intermolecular π–π interactions, **1–3** cannot form highly concentrated solutions.

§ Crystal data of **1**. The measurements were made on a Bruker SMART CCD with Mo-Kα radiation (λ 0.71073 Å) at 294 K. The structure was solved by direct methods and SHELXS-97, and refined by using SHELXL-97. Hydrogen atoms were located at the calculated positions. Absorption correction was applied using SADABS. C<sub>30</sub>H<sub>38</sub>S<sub>12</sub>, M = 783.32, crystal dimension 0.30 × 0.08 × 0.04 mm, triclinic, space group P $\bar{1}$ , a = 5.3630(17), b = 8.9200(3), c = 19.406(6) Å, α = 78.674(5), β = 86.600(6), γ = 85.002(5)°, V = 905.9(5) Å<sup>3</sup>, Z = 1,

D<sub>c</sub> = 1.436 g·cm<sup>-3</sup>, μ = 0.745 mm<sup>-1</sup>, θ range 2.34–26.01°, 4569 reflections collected, 3164 of which were independent (R<sub>int</sub> = 0.0240), GOF = 1.019, 192 parameters, R<sub>1</sub> = 0.0702, wR<sub>2</sub> = 0.1098 for all reflections. Largest diff. peak and hole, 0.348 and -0.363 e·Å<sup>-3</sup>. CCDC 601019. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603632e

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