

ターフェニレン化合物の合成及び溶液プロセスに 適応可能なTFT用ターフェニレン半導体材料

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Synthesis of Terphenylene Compounds and Solution Processable Terphenylene Semiconductors for TFT

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The linear terphenylene (benzo[3,4]cyclobuta[1,2-b]biphenylene) compounds were synthesized from tetrabromoterphenyls with lithiation followed by a four membered ring formation reaction using cupric chloride for the first time. Since the tetrabromoterphenyls were prepared by a palladium-catalyzed coupling reaction, this synthetic method can provide a wide range of symmetric and unsymmetric terphenylene compounds with high rigidity. It is known that the molecular structure of the unsubstituted terphenylene was almost planar and the arrangement of molecules was classified as a herringbone packing such as pentacene. TFTs were fabricated in "top"-contact configuration on the HMDS-treated Si/SiO₂ substrate by vacuum deposition. Terphenylene compounds were purified by recrystallization, used as semiconductors, and we have found for the first time that they had *p*-channel field effect properties. Dibenzoterphenylene and naphthoterphenylene (TC1), which is an isomer of dibenzoterphenylene, exhibited mobilities of 0.0058 and 6.0×10^{-4} cm²/V•s in air, respectively. Introducing substituents to TC1 developed soluble TC2 and TC3. The performance of devices using TC2 and TC3 were highly improved to give mobilities of 0.022 and 0.055 cm²/V•s in air, respectively. Since a device of pentacene had a mobility of 0.033 cm²/V•s in air in the same conditions of fabrication, TC2 and TC3 have comparable performance to pentacene in air. TFT devices using TC2 and TC3 were also prepared by solution process and showed mobilities of 1.3×10^{-4} and 2.9×10^{-3} cm²/V•s, respectively, without detailed investigation of coating conditions.

1 . Introduction

The most important material properties for the organic semiconductors in TFTs are high mobility, stability, and processability. The stability of transistors and semiconductors in solution process under ambient conditions has become increasingly important for practical applications. The organic semiconductors with high performance reported to date are shown in Fig. 1.

Especially, the bis(ethynyl) substituted acenes were reported to afford high performance for solution process¹⁾. Although the possibility of photooxidation of the highly conjugated molecules such as acenes cannot be excluded²⁾, fused ring compounds with long axes are expected to give high performance by increased π -stacking. From the point of view, we focused on the linear terphenylene compounds, which have not been used as organic electronic materials.

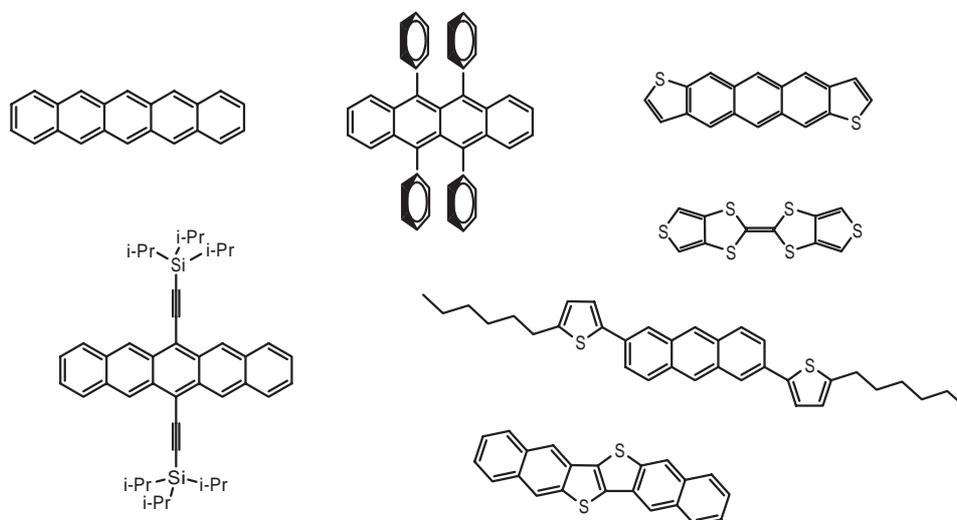


Fig. 1 Organic semiconductors with high performance

We report here the synthesis of terphenylene compounds, the device fabrication, and the FET characteristics.

2 . Synthesis of Terphenylenes

The linear terphenylene (benzo[3,4]cyclobuta[1,2-b]biphenylene) (1) is a known compound³⁾ and adopts a herringbone structure⁴⁾. Since the literature's synthetic method was only limited to unsubstituted and silyl substituted types, we explored the new synthetic route for the more fused types and found that tetrabromoterphenyls underwent lithiation followed by oxidative ring formation reaction using cupric chloride to give the terphenylenes. Since the tetrabromoterphenyls were prepared by a palladium-catalyzed coupling reaction, this methodology can provide a wide range of fused symmetric and unsymmetric terphenylene compounds with high rigidity (Scheme1).

Dibenzoterphenylene (2) and naphthoterphenylene

(TC1), which is an isomer of 2, were synthesized (Fig. 2). In addition, the easily soluble TC2 and TC3, which are alkyl substituted TC1s, were also obtained. These terphenylene compounds were purified by recrystallization. Especially, TC2 and TC3 have good solubility of 0.24 and 0.80 wt% in toluene at 100 °C, respectively, and were recrystallized from toluene to yield orange small crystals.

The UV-vis absorption spectra of vacuum-deposited films of TC1 and TC2 are shown in Fig. 3. While absorption peaks appeared almost at the same

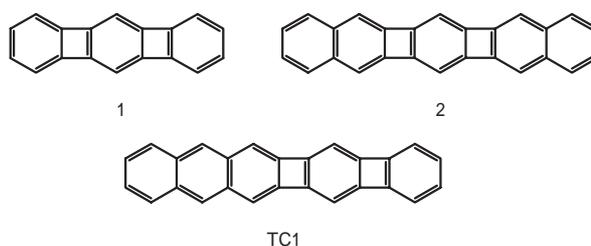
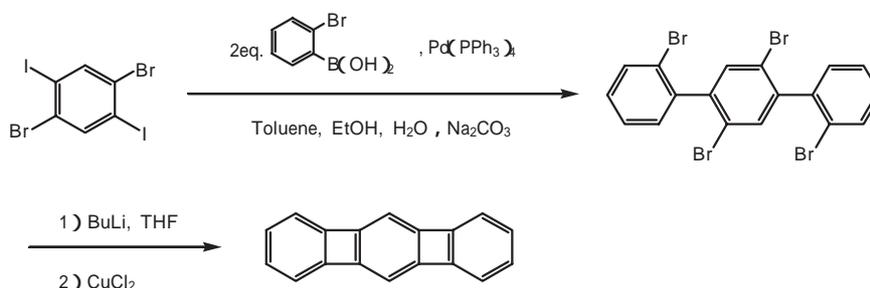


Fig. 2 Terphenylene compounds



Scheme 1 New synthetic method of terphenylenes

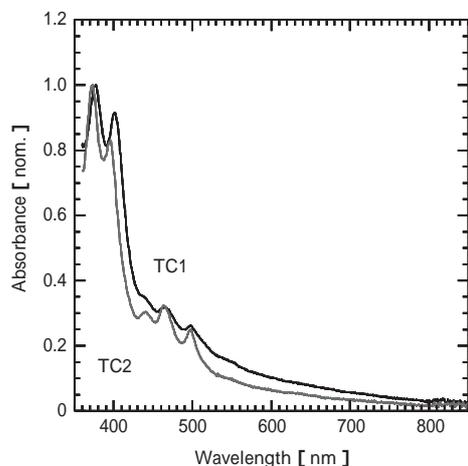


Fig. 3 UV-vis spectra of TC1 and TC2 in thin film

wavelengths, the spectrum of TC2 gave a clearer waveform indicating the thin film of TC2 has less scattering than that of TC1 and the longest absorption at 498 nm. Since the UV-vis absorption spectrum of TC2 in tetrahydrofuran solution showed its longest absorption peak at 489 nm, the 9 nm red shift was observed from solution to a thin film. And the optical band gap of 2.36 eV was estimated from the absorption edge of the spectrum of the thin film. In pentacene, the band gap from the absorption edge around 1.8 eV. Therefore, the band gap of TC2 is significantly higher than that of pentacene, indicating higher redox stability.

3 . Field-Effect Transistors

[1] Device Fabrication

The field effect transistors were fabricated in top-contact configuration on a heavily doped n^+ -Si wafer with a thermally grown oxide layer (200 nm). On the top of the organic thin film, gold drain and source electrodes were deposited to yield devices with a channel length of 15 μm and a channel width of 500 μm . A thin film (50 nm) of terphenylenes as an active layer was vacuum-deposited on the HMDS-treated Si/SiO₂ substrate at room temperature. The TFT devices using TC2 and TC3 were also prepared by solution deposition (spin-coating and drop-casting) of the 0.1 wt% solution (100 or 90 μm) in toluene on the Si/SiO₂ substrate.

[2] Electrical Characteristics

All measurements were performed in air at room

Table 1 Field-effect mobility and on/off ratio for terphenylene compounds in air

compound	mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)	on/off ratio
2	0.0058	5.3×10^3
TC1	6.0×10^{-4}	1.0×10^3
TC2	0.022	2.4×10^6
TC3	0.055	7.1×10^6
pentacene	0.033	6.6×10^2

temperature. All the organic FET devices using the terphenylene compounds showed p -channel FET characteristics except for 1⁵). Field-effect mobilities were calculated from the saturation regime and current on/off ratios were determined from the I_{DS} between $V_{\text{G}} = 0 \text{ V}$ and -40 V . The FET performances of vacuum-deposited films are summarized in Table 1. With little optimization the mobility of dibenzoterphenylene (2) was found to be $0.0058 \text{ cm}^2/\text{V}\cdot\text{s}$. There were no differences between atmospheres measured regarding electrical properties of the device of 2. On the other hand, while the device of TC1 showed an enhanced mobility ($0.019 \text{ cm}^2/\text{V}\cdot\text{s}$) by one order of magnitude in vacuum, the mobility highly decreased in air ($6.0 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$).

When TC2 was used as an active layer, the mobility was increased by two orders of magnitude ($0.022 \text{ cm}^2/\text{V}\cdot\text{s}$) in air compared to that of TC1. In addition, the on/off ratio was also drastically improved from 1.0×10^3 to 2.4×10^6 . In the case of TC3, which is another alkylated TC1 and has a higher solubility than TC2, the device exhibited the mobility as high as $0.055 \text{ cm}^2/\text{V}\cdot\text{s}$ and the on/off ratio of 7.1×10^6 . The device with a vacuum deposition film of pentacene was prepared under the same fabrication conditions as above and the electrical properties were evaluated in air giving a hole mobility of $0.033 \text{ cm}^2/\text{V}\cdot\text{s}$ and an on/off ratio of 6.6×10^2 . Since the mobilities and the on/off ratios by measurement of the devices using TC2 and TC3 in vacuum were the same as or only slightly higher than those in air, it is emphasized that the high performance of TC2 and TC3, which mobilities are comparable to pentacene, is maintained in air. Fig. 4 demonstrates the FET characteristics of the device of TC2.

A FET device using TC2 from solution was also prepared and its electrical properties were calculated. A 0.1 wt % solution of TC2 in hot toluene was spin coated onto the Si/SiO₂ substrate at room temperature. The

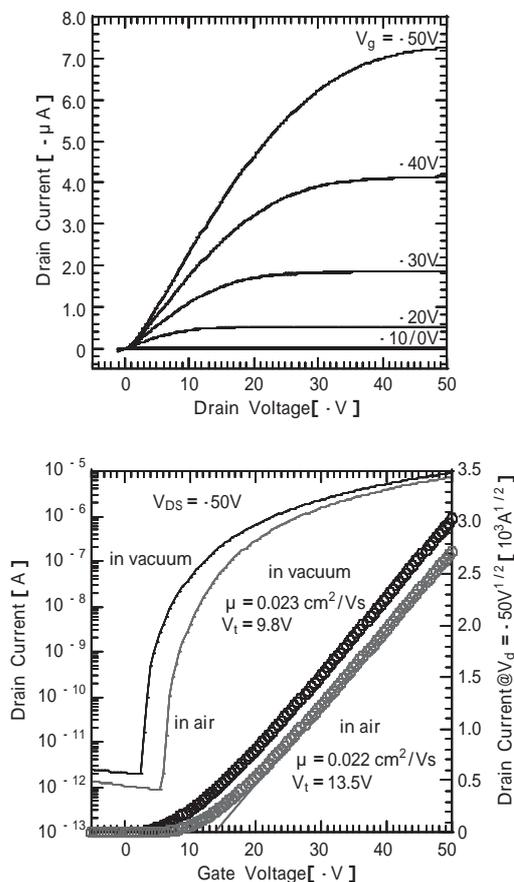


Fig. 4 FET characteristics of devices with vacuum-deposited films of TC2

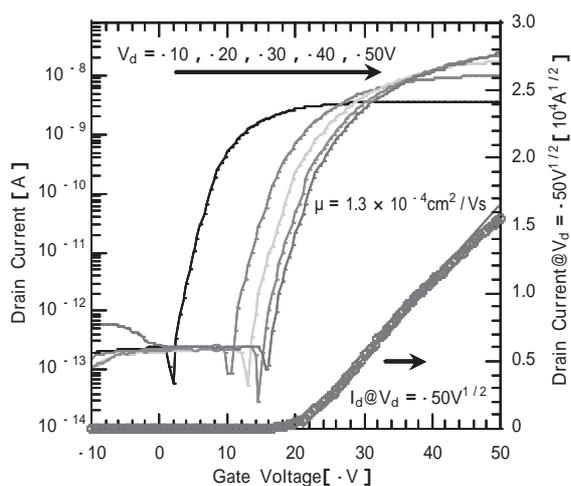


Fig. 5 Transfer characteristics of a device with a solution-deposited film of TC2

solvent was then left to evaporate at room temperature. A field-effect mobility of 1.3×10^{-4} and an on/off ratio of 4.6×10^4 were obtained without detailed investigation of the device fabrication conditions. Fig. 5 shows the FET characteristics of the device obtained by the solution method using TC2.

In the case of TC3, a FET activity was obtained by

drop-casting. A solution of TC3 in toluene at 90 °C was applied onto the Si/SiO₂ substrate at 90 °C and the solvent was left to evaporate. The mobility was increased by one order of magnitude (2.9×10^{-3} cm²/V · s) compared to that of TC2 and the on/off ratio (1.5×10^4) was comparable to TC2.

4 . Conclusions

The new highly fused terphenylene compounds such as 2 and TCI-3 were synthesized by the coupling method with cupric chloride and the organic FET devices using these terphenylenes as an active layer were fabricated. We found that the devices using these terphenylene compounds exhibited *p*-type transistor responses for the first time. Especially, the devices using TC2 and TC3 gave not only comparable mobilities to that of pentacene but also high current on/off ratios even in air. Therefore, fused terphenylene compounds are thought to have the same potential of electrical properties as pentacene and the much higher stability. Although the mobilities in solution process have not been high enough yet, alkylated TCIs (TC2 and TC3) have high solubility in toluene and gave the devices bearing a FET activity. We will continue to examine the optimization of the structure of terphenylene compounds that is utilized for practical printing process.

5 . Experimental

[1] General procedure for synthesis of tetrabromoterphenyl

A nitrogen 100 ml schlenk flask was charged with 1,4-dibromo-2,5-diiodobenzene (4.39 g, 9.00 mmol), tetrakis(triphenylphosphine)palladium (974 mg, 0.84 mmol), 2-bromophenylboronic acid (Aldrich, 4.16 g, 20.7 mmol), toluene (72 ml), ethanol (18 ml), and an aqueous solution (22 ml) of sodium carbonate (5.72 g, 54.0 mmol) under nitrogen. The mixture was stirred at 85 °C for 15 h. After cooling to room temperature, dichloromethane and brine were added, and the organic layer was separated and concentrated under reduced pressure. The residue was recrystallized from toluene to give 4.18 g (85% y) of white needle crystals of 2,2',5',2''-tetrabromo-1,1',4',1''-terphenyl.

[2] General procedure for synthesis of terphenylene

A nitrogen 100 ml schlenk flask was charged with 2,2',5',2''-tetrabromo-1,1',4',1''-terphenyl (269 mg, 0.492 mmol) prepared above and tetrahydrofuran (23 ml) under nitrogen. After cooling to -80 °C, sec-butyllithium (cyclohexane solution of 0.98M) (5.0 ml, 4.9 mmol) was added. The mixture was stirred for 20 min and copper (II) chloride (828 mg, 6.20 mmol) was added at -75 °C. The mixture was gradually warmed to room temperature. After brine and toluene were added, the resulting organic layer was separated, washed with brine, and concentrated under reduced pressure. The residue was washed with hexane and recrystallized from toluene to give 24.0 mg (22% yield) of red crystals (plates) of terphenylene.

6 . Acknowledgement

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7 . References

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