A soluble bispentacenequinone precursor for creation of directly 6,6′-linked bispentacenes and a tetracyanobipentacenequinodimethane

Kazuki Tanaka, a Naoki Aratani, a,b Daiki Kuzuhara, c Sadaaki Sakamoto, c Tetsuo Okujima, c Noboru Ono, c Hidemitsu Uno a and Hiroko Yamada a,d

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

We have synthesized 13,13′-(3,5-bis(trifluoromethyl)phenyl)-6,6′-bipentacene from a soluble bispentacenequinone precursor. Bispentacene takes orthogonal conformation in the solid state and exhibits four reversible redox potentials. In addition, a tetracyanobipentacenequinodimethane was obtained for the first time from the pure bispentacenequinone.

Introduction

Organic molecular materials have attracted great interest in recent years as a potential low-cost alternative to amorphous silicon-based semiconductors for many applications in electronics. 1 Among these, the electronic properties of pentacene are exceptionally well investigated, making it a common benchmark in the field of organic electronic devices. 2 The pentacene oligomers, however, remain virtually unexplored, mainly because of their chemical instability and low solubility. Hitherto only two examples of pentacene dimers were so far reported. 3,4

A potential precursor of bispentacene is bispentacenequinone 2 (Scheme 1). Surprisingly, however, 2 has been “unavailable” even its simple structure, since the conventional synthetic route for 2 is via oxidation of pentacenone 1, which results in the formation of an inseparable mixture of 2 and pentacenequinone 3 due to their low solubility. 3,5 Thus, soluble precursors with thermally or photochemically removable leaving groups have intrinsically merited. 6–10 Recently we have reported the photochemical conversion in solutions or in films of an α-diketone precursor into the corresponding acene with the release of two CO molecules. 9,11 Beside them, thermal reaction has also been applied to the synthesis of larger acenes by taking advantage of the unique features of bicyclo[2.2.2]octadiene (BCOD). 12 Such a thermal method has enabled us to prepare benzoporphyrinoids which can be used as materials for the solar cell and the organic field effect transistor (OFET) devices. 13

Now we describe the synthesis of directly 6,6′-linked bispentacene via the retro-Diels–Alder reaction of BCOD-bispentacene precursors (Scheme 2). Our work on soluble oligoacene precursors has shown that, in addition to providing increased solubility and chemical stability, the crystalline nature becomes remarkable. We here also report the application of our precursor method to the synthesis and characterization of an extended tetracyanobipentacenequinodimethane (TCNQ) derivative, tetracyanobipentacenequinodimethane (TBPQ, 11).


Results and discussion

Synthesis of directly 6,6′-linked bispentacene

The route for the synthesis of BCOD-bispentacenequinone precursor 7 starts from a Diels–Alder reaction of p-benzoquinone with 5,6-dimethylene-bicyclo[2.2.2]oct-2-ene (4) to form the bisadduct, then subsequent dehydrogenation provided the bicycloanthraquinone 5 (Scheme 2). 14 The quinone 5 was reduced with lithium aluminium hydride (LAH) and the anthrone 6 obtained was oxidized by the Matur’s conditions to get bianthrone 7 in 77% yield. 15 As expected, 7 is soluble in common organic solvents (>5 mg/ml in CHCl 3 ) so that it would be a versatile reagent for many reactions (vide infra).

The structure of 7 was confirmed by its 1H-NMR and high-resolution electrospray ionization time-of-flight (HR-ESI-TOF) mass spectroscopies (Supporting Information). Slow vapour diffusion of methanol into a chloroform solution of 7 gave its good crystals suitable for X-ray diffraction analysis (Figure 1). 1,7 The crystal structure of 7 revealed a butterfly-shaped skeleton unambiguously, in which the anthracene core is distorted into a saddle conformation.

At first, we tried to prepare an authentic bispentacene from 7 as a non-substituted mother skeleton. After several optimization
experiments, we found that the stepwise reduction of 7 with LAH and then DIBAL gave 8a in 31% yield. The structure of 8a was revealed by a single-crystal X-ray diffraction analysis (Figure 1c).\textsuperscript{1} In the crystal, the two pentacene units in 8a display a perpendicular conformation of about 88°. Then we performed the retro-Diels–Alder reaction of 8a. The thermogravimetric (TG) analysis of 8a is shown in Figure S15. The weight loss of 8a started at around 250°C and stopped after 300°C. Although the weight loss of 8a was 15% that corresponds to the elimination of four ethylene molecules, its \textsuperscript{1}H-NMR, ESI-TOF mass, and UV-vis absorption spectroscopies indicated that a lot of undesired compounds were produced after the formation of 9a, suggesting the chemical instability of 9a (Figures S16 and S17). Next, with 13,13′-free bispentacene precursor 8a in hand, we thus examined its halogenation for metal-catalyzed cross-coupling reactions.

Though the bromination of 8a proceeded with NBS in THF to provide 8b, unfortunately the yield was as low as 19% (Figure 1d).\textsuperscript{2} It is noteworthy that 8b can be a potential unit for making graphene nano-ribbons.\textsuperscript{16}

![Diagram of compounds](image)

Scheme 2. Synthesis of bispentacenes 9a-d. Reaction conditions: a) i) CHCl\textsubscript{3}, ii) KOH/EtOH, 60% (2 steps). b) Lithium aluminium hydride (LAH), then 6 N HCl, THF, 66%. c) Pyridine-N-oxide, piperidine, FeSO\textsubscript{4}, pyridine, 80%. d) LAH, then 6 N HCl, DIBAL 31% (2 steps) for 8a, ArLi then Na\textsubscript{2}HPO\textsubscript{4}, NaI for 8c (67%) and 8d (28%), e) NBS, 19%, f) heating, 93% for 9d.

As has been extensively demonstrated in the pentacene chemistry, its stability should depend on the substituents on the periphery.\textsuperscript{17} So we next tried to synthesize the 13,13′-bis-arylated bispentacenes. Treatment of 7 with phenyllithium, subsequent deoxygenation and aromatization with sodium iodide and sodium hypophosphite,\textsuperscript{18} gave the bispentacene precursor 8c in 46% yields (Figure 1e).\textsuperscript{1} The retro-Diels–Alder reaction of 8c afforded almost pure 9c judging from its TG analysis, \textsuperscript{1}H-NMR, HR-ESI-TOF mass, and UV-vis absorption spectroscopies (Figures S19-22), while it was difficult to remove a small amount of byproducts. Finally, a good electron withdrawing substituent, 3,5-bis(trifluoromethyl)phenyl group was introduced. 8d was prepared by the same method to 8e (Figure 1f).\textsuperscript{1} 8d smoothly underwent thermal conversion at 300°C for 10 min, and after the measurement of TG, the pure, stable, and soluble 9d was obtained at last without any problems like a zoo of byproducts for 9a-c. We assume that the electron withdrawing groups make the molecule tougher against oxidative ambient conditions owing to the stabilized HOMO level. The structure of 9d is fully consistent with the spectroscopic data. HR-ESI-TOF mass spectrum detected the parent ion peak at m/z = 978.371 (calcd for C\textsubscript{38}H\textsubscript{20}N\textsubscript{4} = 978.216 [M]+) (Figure S13). The \textsuperscript{1}H NMR spectrum of 9d in CD\textsubscript{2}Cl\textsubscript{2} exhibits aromatic protons at 8.32, 7.85, 8.77, 7.30, 7.21, and 7.07 ppm. The structure of 9d was unambiguously determined by single crystal X-ray diffraction analysis (Figures 1g and 1h).\textsuperscript{1} Pentacene planes are highly planar and exhibit a small tilting dihedral angle from orthogonal conformation (78°). Importantly, in the crystal, a pair of slipped π-π stacking of both pentacene planes in 9d results in the formation of two-dimensional grid-like network structure along a-b plane of crystal lattice (Figure 2). This is a new potential structural motif for pentacene based semi-conducting materials.\textsuperscript{2}

This journal is © The Royal Society of Chemistry [year]
The influence of the charge of first pentacene unit in bispentacene should arise from the ferrocene/ferrocenium ion couple as fully reversible waves by cyclic voltammetry (CV). The CV of 9d in CHCl₃ displays four redox potentials at –1.79, –1.72, 0.32, and 0.46 V (vs ferrocene/ferrocenium ion couple) as fully reversible waves (Figure 4). These split one-electron oxidations and reductions for each pentacene unit in bispentacene should arise from the influence of the charge of first-generated pentacene radical ion. The electrochemical HOMO–LUMO gap is thus 2.04 eV.

UV-vis absorption spectra of 8d and 9d along with pentacene are shown in Figure 3. Compared to pentacene (λmax = 578 nm in CHCl₃), 9d exhibits distinctly red-shifted absorption at 612 nm (ε = 2.0 × 10⁴ M⁻¹ cm⁻¹; optical HOMO–LUMO gap is 2.02 eV) with the vibrational bands and a small stokes shift (159 cm⁻¹), indicating a considerable electronic communication between two pentacene units with rigid skeleton in 9d. This is also confirmed by cyclic voltammetry (CV). The CV of 9d in CHCl₃ displays four redox potentials at –1.79, –1.72, 0.32, and 0.46 V (vs ferrocene/ferrocenium ion couple) as fully reversible waves (Figure 4). These split one-electron oxidations and reductions for each pentacene unit in bispentacene should arise from the influence of the charge of first-generated pentacene radical ion. The electrochemical HOMO–LUMO gap is thus 2.04 eV.

Synthesis of tetracyanobipentacenequinodimethane (TBPQ)

The successful creation of bispentacene 9d from bipentacenequinone 7 made us aware that the soluble precursor 7 could be available for synthesis of other “insoluble” products. Thus, we tried to synthesize an extended TCNQ analogue, tetracyanobipentacenequinodimethane (TBPQ) 11 (Scheme 3). In recent years, much efforts have been made to develop new electron acceptor molecules whose structures would enhance the electrical conductivities in their molecular electronic devices. Among these, TCNQ has been widely used as an acceptor molecule to form highly conducting charge transfer complexes. The simple extension of the π-system of TCNQ has been shown to lead to a regulation of the intra- and intermolecular Coulomb repulsion in their dianion forms. However, one often confronts a dilemma that an electron-deficient π-expanded molecule has low solubility in common organic solvents, which hampers the isolation and the characterization of the desired compounds.

Taking advantage of the soluble character of 7, first we tested a condensation reaction of 7 with malononitrile (Scheme 3). The reaction in the presence of TiCl₄ as catalyst was successful in pyridine and toluene at high temperature, affording 10 in 10% yield. As expected, 10 is soluble in various solvent and the structure was confirmed by its ¹H-NMR and HR-ESI-TOF mass spectrosocopies, and single crystal X-ray diffraction analysis. The crystal structure of 10 revealed a butterfly-shaped skeleton unambiguously, in which the dicyanomethylene groups are deviated from the anthracene mean plane due to the steric hindrance by the hydrogen atoms at the peri-positions (Figure 5). The planes NC-C-CN and the central benzene ring make an angle of 35.0°. The deviation between two mean planes of the central benzene ring is 1.40 Å. Unfortunately, however, the thermal reaction of 10 afforded unidentified products so that we changed the synthetic route.
With the pure bispentacenequinone, the isolation of TBPQ crystal structures clearly indicate the flexibility of polymorphism (Figure S25). The characterization of a pyrolytic compound reaction started at around 200°C, and we observed the retro-Diels–Alder reaction at around 250°C (Figure S25). The characterization of a pyrolytic compound obtained quantitatively was successfully done, the structure of which is shown in Figure 5. Interestingly, the quinone 2 exhibits polymorphism (Figure 6 and Figure S37). The side views of these crystal structures clearly indicate the flexibility of bispentacenequinone framework. This is the first practical isolation of bispentacenequinone 2.

From TG analysis of 7, we observed the retro-Diels–Alder reaction started at around 200°C and ended at around 250°C (Figure S25). The characterization of a pyrolytic compound obtained quantitatively was successfully done, the structure of which is shown in Figure 5. Interestingly, the quinone 2 exhibits polymorphism (Figure 6 and Figure S37). The side views of these crystal structures clearly indicate the flexibility of bispentacenequinone framework. This is the first practical isolation of bispentacenequinone 2.

With the pure 2 in hand, a condensation reaction of 2 was performed with malononitrile, affording 11 in 10% yield. Although the solubility of 11 is limited, the structure of 11 is fully consistent with the spectroscopic data. HR-ESI-TOF mass spectrum detected the parent ion peak of 11 at m/z = 680.201 (calcd for C_{38}H_{24}N_{4} = 680.200 [M⁺]) (Figure S14). The ¹H NMR spectrum of 11 in CDCl₃ exhibits aromatic protons at 8.71, 8.01, 7.77, 7.54, and 7.41 ppm.

The CV measurements of the new compound 11 along with 10 and tetracyanopentacenequinodimethane have been carried out in THF at room temperature. TBPQ 11 exhibits one reversible single-wave reduction at −1.51 V, implying the electron storage ability of 11 (Figure S28). Deep negative shift of the reduction potential of 11 compared to that of tetracyanopentacenequinodimethane (−1.06 V, Figure S28) indicates that the elongation of the distance between dicyanomethylene units by pentacene makes its electron accepting ability moderate.

**Conclusions**

In summary, we have synthesized 13,13′-bis(trifluoromethyl)phenyl)-6,6′-bipentacenequinodimethane (11) from the soluble bispentacenequinone precursor 7. 9d takes orthogonal conformation and 2D grid-like network in the solid state, and exhibits four reversible redox potentials. In addition, TBPQ 11 was obtained for the first time from the pure bispentacenequinone 2. A series of TCNQs have received much electrochemical attention; however, there was insufficient data to actually measure it. Its instability, combined with poor solubility, has made its preparation and study difficult. Soluble precursor method leads us to believe that this strategy enables the preparation of higher acenes with the improved stability and solubility. Complexation study of TBPQ with various donors is now under way.

**Acknowledgements**

This work was partly supported by Grants-in-Aid for Scientific Research (No. 22350083) and for Young Scientists (A) (No. 23685030), the Green Photonics Project in NAIST supported by MEXT, and CSTP initiated FIRST program (No. 22350083) by JSPS. We thank Mr. S. Katao, NAIST, for the X-ray diffraction analysis and Ms. Y. Nishiyama, Ms. Y. Nishikawa, and Ms. M. Yamamura, NAIST, for the mass spectroscopy measurements.

**Notes and references**

- Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), Takayama-cho, Ikoma, Nara 630-0192 Japan. Fax: +81-743-72-6042; Tel: +81-743-72-6030; E-mail: atani@ms.naist.jp
- PRESTO, Japan Science and Technology Agency (JST).
- Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Bunkyo-cho 2–5, Matsuyama, 790–8577 Japan.
- CREST, Japan Science and Technology Agency (JST).
- Electronic Supplementary Information (ESI) available: Experimental details of the synthesis and spectroscopic analytical data of new compounds. For ESI and crystallographic data in CIF or other electronic format. See DOI: 10.1039/b000000x.
- Crystallographic data for 7: C_{38}H_{24}O_{2}, Mω = 696.89, monoclinic, space group P2₁/n (No. 14), a = 10.2853(4), b = 12.1795(4), c = 14.7576(5) Å, \( β = 106.4150(10)° \), \( V = 1773.34(10) Å³ \), \( ρ_{calc} = 1.305 \) g/cm², Z = 2, R₁ = 0.0668 [I > 2σ(I)], Rw = 0.1868 (all data), GOF = 1.060.
Cry6tallographic data for 8a: C$_{36}$H$_{32}$O$_{2}$(H$_2$O)$_3$, Mr = 740.98, triclinic, space group P-1 (No. 2), a = 11.984(5), b = 11.3073(5), c = 16.8154(7) Å, α = 73.8090(10), β = 86.8410(10), γ = 75.5400(10), V = 1979.44(15) Å$^3$, ρ$_{\text{calcd}}$ = 1.243 g/cm$^3$, Z = 2, R$_I$ = 0.0697 [I > 2σ(I)], Rp$ _{\text{w}}$ = 0.2343 (all data), GOF = 1.055. Crystalline data for 8b: C$_{23}$H$_{24}$Br$_2$-0.58(2)CHCl$_3$. Mr = 914.38, monoclinic, space group C2/c (No. 15), a = 41.9304(4), b = 15.3835(14), c = 18.8623(18) Å, β = 102.9120(10)°, V = 11859.0(19) Å$^3$, ρ$_{\text{calcd}}$ = 1.536 g/cm$^3$, Z = 12, R$_I$ = 0.0994 [I > 2σ(I)], Rp$ _{\text{w}}$ = 0.3153 (all data), GOF = 1.040.

Crystallographic data for 8c: C$_{36}$H$_{33}$O$_2$(CHCl$_3$), Mr = 1177.14, monoclinic, space group P2$_1$/c (No. 14), a = 24.018(3), b = 10.2100(14), c = 22.022(3) Å, β = 90.352(2)°, V = 5401.5(4) Å$^3$, ρ$_{\text{calcd}}$ = 1.448 g/cm$^3$, Z = 4, R$_I$ = 0.0774 [I > 2σ(I)], Rp$ _{\text{w}}$ = 0.2429 (all data), GOF = 1.015. Crystallographic data for 8d: C$_{23}$H$_{24}$F$_2$(CHCl$_3$), Mr = 1568.52, monoclinic, space group C2/c (No. 15), a = 24.6901(5), b = 21.1291(5), c = 17.5492(4) Å, β = 130.4530(10)°, V = 69664.4(6) Å$^3$, ρ$_{\text{calcd}}$ = 1.496 g/cm$^3$, Z = 4, R$_I$ = 0.0693 [I > 2σ(I)], Rp$ _{\text{w}}$ = 0.2151 (all data), GOF = 1.064. Crystallographic data for 8e: C$_{23}$H$_{24}$F$_2$(CHCl$_3$), Mr = 978.84, monoclinic, space group C2/c (No. 15), a = 13.271(10), b = 30.352(4), c = 12.823(3) Å, β = 121.152(11)°, V = 4420.6(1) Å$^3$, ρ$_{\text{calcd}}$ = 1.471 g/cm$^3$, Z = 4, R$_I$ = 0.1051 [I > 2σ(I)], Rp$ _{\text{w}}$ = 0.3304 (all data), GOF = 1.035. Crystallographic data for 10: C$_{36}$H$_{35}$N$_2$(CHCl$_3$), Mr = 1031.68, monoclinic, space group C2/c (No. 15), a = 17.4912(6), b = 12.3477(4), c = 23.7674(8) Å, β = 93.3020(10)°, V = 51247.3(13) Å$^3$, ρ$_{\text{calcd}}$ = 1.337 g/cm$^3$, Z = 4, R$_I$ = 0.0685 [I > 2σ(I)], Rp$ _{\text{w}}$ = 0.1949 (all data), GOF = 1.059. Crystallographic data for 2: C$_{36}$H$_{32}$O$_2$(CHCl$_3$), Mr = 704.00, monoclinic, space group C2/c (No. 15), a = 24.8385(6), b = 11.3087(2), c = 12.6953(19) Å, β = 112.6680(10)°, V = 3290.54(13) Å$^3$, ρ$_{\text{calcd}}$ = 1.421 g/cm$^3$, Z = 4, R$_I$ = 0.0584 [I > 2σ(I)], Rp$ _{\text{w}}$ = 0.1529 (all data), GOF = 1.070. CCDC-923523 (7), 928355 (8a), 928356 (8b), 928358 (8c), 928354 (8d), 928357 (9d), 928349 (10), and 923850 (12) contain the supplementary crystallographic data for this paper.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.