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Electron- or Hole-Transporting Nature Selected by Side-Chain-Directed π-Stacking Geometry: Liquid Crystalline Fused Metalloporphyrin Dimers

Tsuneaki Sakurai,[†] Kentaro Tashiro,[‡] Yoshihito Honsho,[§] Akinori Saeki,[§] Shu Seki,[§] Atsuhiro Osuka,[∥] Atsuya Muranaka,[#] Masanobu Uchiyama,[#,⊥] Jungeun Kim,[▽] Sunyeo Ha,[⊗] Kenichi Kato,[¶] Masaki Takata,[▽,⊗,¶] and Takuzo Aida*[,†]

[†]School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[‡]National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[§]Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
[∥]Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan
[#]Institute of Physical and Chemical Research, RIKEN, 2-1 Hirosawa, Wako-shi, Saitama 351-0198, Japan
[⊥]Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[▽]Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan
[⊗]Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8561, Japan
[¶]RIKEN SPring-8 Center, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

Supporting Information

ABSTRACT: Novel liquid crystalline (LC) semiconductors were prepared from the copper complex of a fused porphyrin dimer as the electroactive core by attaching to its periphery dodecyl and semifluoroalkyl side chains site-specifically (**P**≡**P**$_{hetero}$) and semifluoroalkyl side chains alone (**P**≡**P**$_{homo}$). The former and latter formed rectangular columnar and orthorhombic LC mesophases, respectively, where the stacking geometries of the π-conjugated core are quite different from one another. Although the π-electronic properties of the core units in **P**≡**P**$_{hetero}$ and **P**≡**P**$_{homo}$ in solution are substantially identical to one another, transient photocurrent profiles of their LC states under time-of-flight conditions clearly showed that **P**≡**P**$_{hetero}$ behaves as an n-type semiconductor, whereas **P**≡**P**$_{homo}$, in contrast, behaves as a p-type semiconductor.

In general, whether organic semiconductors transport electrons or holes has been considered to be determined mostly by the intrinsic redox properties of their constituent electroactive molecules.[1] Therefore, diversification of the range of n- and p-type organic semiconductors totally relies on the development of new π-conjugated structural motifs.[2] Toward this general understanding, we report here that, by tailoring assembly-directing side chains, both n- and p-type liquid crystalline (LC) semiconductors can be obtained from a single π-conjugated motif.

The electroactive core unit employed in the present work is the Cu complex of a triply fused porphyrin dimer adopting a characteristic oblong disk shape (Figure 1). Triply fused metalloporphyrin oligomers are interesting π-conjugated motifs, particularly for photovoltaic applications, because of their extraordinary high absorptivities toward sunlight, covering from ultraviolet up to near-infrared wavelength regions.[3] In 2008, we reported the first LC version of this family, which carries dodecyl side chains on one Cu porphyrin unit and triethylene glycol (TEG) side chains on the other.[4] This particular heterotropic design was essential for the liquid crystal formation, since a prototype of this compound carrying only dodecyl side chains did not form a LC assembly but rather an amorphous solid. Although most porphyrin-based materials have been reported to show a hole-transporting property,[5] the above LC material, in contrast, behaved as an n-type semiconductor.[4] In the present work, this unexpected observation prompted us to investigate if the electron-transporting nature of this material is intrinsic to the core unit of the LC molecule or its particular peripheral design. In order to address this issue,we newly synthesized heterotropically fused **P**≡**P**$_{hetero}$ along with homotropic **P**≡**P**$_{homo}$ (Figure 1) by using semifluoroalkyl side chains instead of the TEG chains,[6] since fluorinated hydrocarbons are immiscible, just like TEG, with hydrocarbons and also have a very strong self-assembling nature.[7] Fortunately, both compounds formed a LC mesophase with a π-stacked columnar structure. However, to our surprise, their preferences for carrier species were totally opposite to one another.

Differential scanning calorimetry (DSC; Figure S4) of **P**≡**P**$_{hetero}$, on its second heating, displayed a LC mesophase ranging from −26 to 163 °C (Figure 1). This LC temperature range is much wider than that of its TEG version (−17 to 99 °C) previously reported.[4] Likewise, **P**≡**P**$_{homo}$ formed a LC mesophase in a temperature range from −32 to 199 °C (Figures 1 and S4). Polarized optical microscopy (POM) of both **P**≡**P**$_{hetero}$ (Figure 2a) and **P**≡**P**$_{homo}$ (Figure 2b) showed a clear dendritic texture typical of columnar LCs. In X-ray diffraction (XRD) analysis upon synchrotron radiation, **P**≡**P**$_{hetero}$ at 30 °C displayed an

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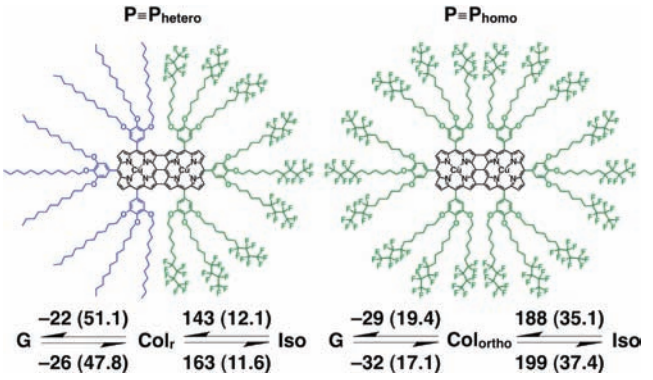

Figure 1. Molecular structures and phase transition temperatures (°C) of copper complexes of fused porphyrin dimers **P≡P$_{hetero}$** and **P≡P$_{homo}$**. Transition enthalpies (kJ mol^{-1}) are given in parentheses.

intense diffraction peak at 2θ = 1.05° (d = 59.1 Å) along with several minor peaks in a wider-angle region (Figure 2c and Table S1). As in the case of the heterotropic TEG version,[4] these diffractions were successfully indexed to a 2D rectangular lattice with a symmetry group of *p2mg*,[8] where lattice parameters a and b were 59.1 and 32.5 Å, respectively (Figure S3). In sharp contrast, **P≡P$_{homo}$** carrying semifluoroalkyl side chains alone at 170 °C showed a crystal-like diffraction pattern (Figure 2d and Table S1), which was indexed to a 3D orthorhombic lattice[9] with lattice parameters a, b, and c of 70.9, 28.4, and 20.1 Å, respectively. Due to their LC characters, both **P≡P$_{hetero}$** and **P≡P$_{homo}$** in ther mesophases are shearable.[9b]

By means of variable-temperature absorption spectroscopy in the film state, we found that the π-stacking geometries of the fused Cu porphyrin core in these LC mesophases are different from each other. Porphyrin derivatives are known to change their absorption spectral profiles upon π-stacking.[10] An isotropic melt of **P≡P$_{hetero}$** at 150 °C showed two characteristic Soret absorption bands at 407 and 561 nm (Figure 2e, red).[3] When the hot melt of **P≡P$_{hetero}$** was cooled to allow the isotropic-to-LC phase transition, a color change from dark purple to reddish brown resulted. Accordingly, the longer-wavelength Soret band, on stepwise cooling from 150 to 125 °C, showed a 10-nm blue shift hypochromically. This spectral change took place abruptly around the phase transition temperature (Figure 2e). All these features are analogous to those observed for the TEG version of **P≡P$_{hetero}$**.[4] Although the absorption spectral profile of an isotropic melt of **P≡P$_{homo}$** at 205 °C (Figure 2f, red), displaying two Soret bands at 407 and 564 nm, was just like that of **P≡P$_{hetero}$** (*vide ante*), the spectra of these compounds in the LC state were quite different from one another. When **P≡P$_{homo}$** was cooled to 185 °C to allow the isotropic-to-LC phase transition, its Soret bands both became less intense (Figure 2f). Furthermore, in sharp contrast with the case of **P≡P$_{hetero}$**, the longer-wavelength Soret band exhibited an 8-nm red shift, with a new shoulder around 660 nm. Hence, it is clear that the π-stacking geometry of **P≡P$_{homo}$** in the LC state differs from that of **P≡P$_{hetero}$**.

π-Conjugated molecules usually stack with an offset geometry in order to minimize repulsion of π-clouds.[11] Considering the heterotropic and homotropic substitution patterns of these LC molecules, along with reported examples with monomeric porphyrins,[12] we suggest columnar structures (a) and (b) in Figure 3 for **P≡P$_{hetero}$** and **P≡P$_{homo}$** in the LC state, respectively, where

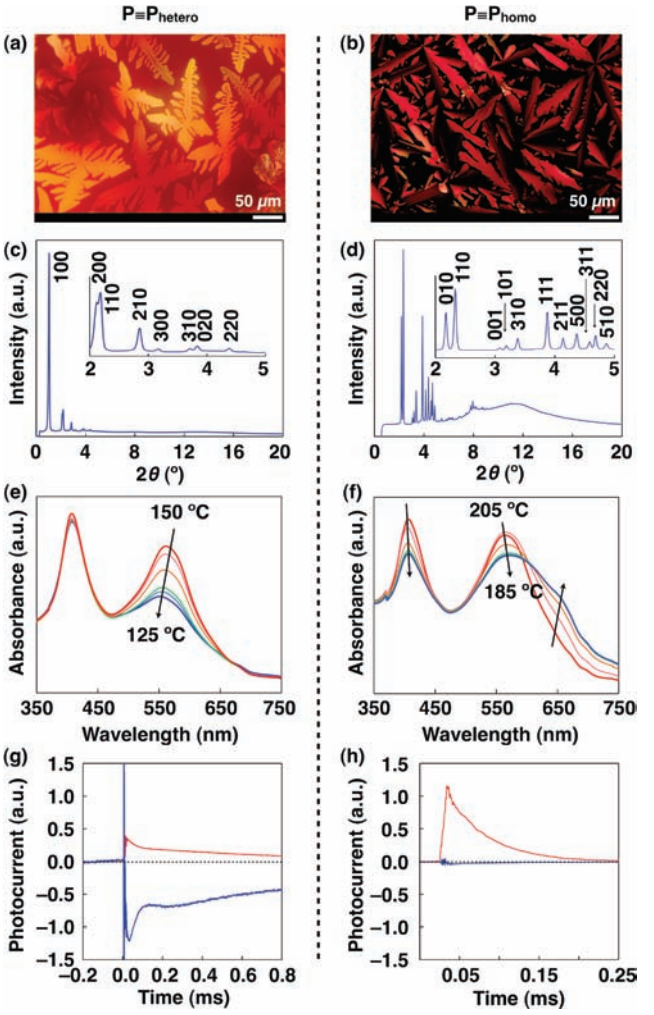

Figure 2. Characterization and properties of **P≡P$_{hetero}$** and **P≡P$_{homo}$** in their liquid crystalline (LC) mesophases. Polarized optical micrographs of (a) **P≡P$_{hetero}$** at 150 °C and (b) **P≡P$_{homo}$** at 185 °C. X-ray diffraction patterns of (c) **P≡P$_{hetero}$** at 30 °C and (d) **P≡P$_{homo}$** at 170 °C. The wavelength of incident X-ray was 1.08 Å. Changes in absorption spectra of (e) **P≡P$_{hetero}$** on cooling from 150 to 125 °C and (f) **P≡P$_{homo}$** on cooling from 205 to 185 °C. Typical transient photocurrent profiles at 25 °C of (g) **P≡P$_{hetero}$** (sample thickness, 3.3 μm; electric field, 0.94 × 10^4 V cm^{-1}) and (h) **P≡P$_{homo}$** (sample thickness, 19 μm; electric field, 6.0 × 10^4 V cm^{-1}) for electron (blue) and hole (red).

column (a) is formed by offset stacking of the π-conjugated core with a "slipped geometry", while column (b) is formed by offset stacking of the π-conjugated core with a "twisted geometry". As discussed already for the TEG version of **P≡P$_{hetero}$**,[4] which forms a rectangular columnar mesophase just as **P≡P$_{hetero}$**, column (a) seems to be the only possible structure that can cope with both stacking of the π-conjugated core and segregation of its two incompatible side chains. On the other hand, the twisted geometry in column (b) is a likely candidate for homotropically substituted **P≡P$_{homo}$**, since it allows for the formation of a continuous array of the highly self-associating semifluoroalkyl side chains around the column. In contrast, this geometry is unlikely for **P≡P$_{hetero}$**, because segregation of the two incompatible side chains is not allowed. Based on spectral simulation,[6] a dimer model for column (a) with a slipped geometry suggests

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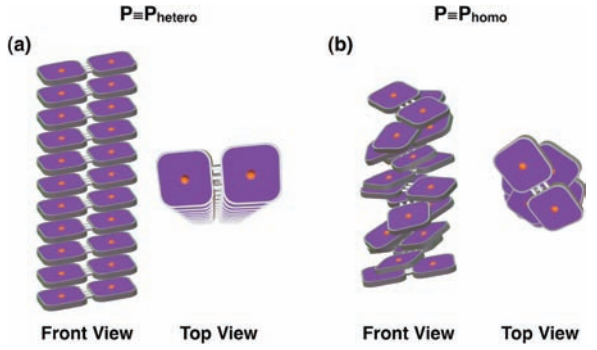

Figure 3. Schematic illustrations of the columnar structures (π-stacked core parts) proposed for the (a) rectangular and (b) orthorhombic columnar LC mesophases of **P≡P$_{hetero}$** and **P≡P$_{homo}$**, respectively. Judging from the XRD patterns (Figure 2c,d), the LC columns of **P≡P$_{homo}$** and **P≡P$_{hetero}$** are likely disordered along the columnar axis.

a blue shift of the Soret band, as observed for assembled **P≡P$_{hetero}$**, when the translational operation is made along the shorter axes of the π-conjugated units (Figure S5). If this operation is made along the longer axes, a blue shift can be expected only when the displacement is marginal (Figure S6). On the other hand, a π-stacked dimer model for column (b) with a twisted geometry suggests a spectral red shift, as observed for assembled **P≡P$_{homo}$**, when the dihedral angle lies in a range of 60−90° (Figure S7).[4]

We measured photocurrent profiles of **P≡P$_{hetero}$** and **P≡P$_{homo}$** in their LC states (25 °C) using a time-of-flight (TOF) technique. As shown in Figure 2g (blue), **P≡P$_{hetero}$** displayed an explicit n-type semiconducting character, where the electron mobility under an applied electric field of 0.94×10^4 V cm^{-1} was evaluated as 1.3×10^{-3} cm^2 V^{-1} s^{-1} (Figure S8).[6] Although the TOF profile also showed a small p-type signature, the photocurrent was too small to evaluate.[13] To our surprise, **P≡P$_{homo}$**, in sharp contrast with **P≡P$_{hetero}$**, behaved as a p-type semiconductor. In the TOF profile of **P≡P$_{homo}$** in its LC mesophase, a photocurrent appeared only when the applied electrical bias was positive (Figure 2h, red). In accordance with this observation, transient absorption spectroscopy (TAS)[14] of **P≡P$_{homo}$** (Figure S12) showed an absorption band around 690 nm, which can be assigned to radical cation species **P≡P$_{homo}^{\bullet+}$** by reference to the differential spectral profile between chemically generated **P≡P$_{homo}^{\bullet+}$** and neutral **P≡P$_{homo}$** (Figure S12).[6] The hole mobility, observed at an electric field strength of 6.0×10^4 V cm^{-1} in the TOF experiment, was evaluated as 4.3×10^{-3} cm^2 V^{-1} s^{-1} (Figure S8).[6] From these observations, whether the fused Cu porphyrin dimer core transports electron or hole in the LC state appears to be determined by its side chains.

In a good solvent such as $CH_2Cl_2/C_6H_5CF_3$ (2/1 v/v), the absorption spectral profile (Figure S13) and differential pulse voltammogram (Figure S14) of **P≡P$_{hetero}$** were little different from those of **P≡P$_{homo}$**,[6] indicating that the intrinsic electronic properties of their core units are substantially identical to one other. Hence, the n- and p-type semiconducting natures, observed for the LC states of **P≡P$_{hetero}$** and **P≡P$_{homo}$**, respectively, most likely originate from the different geometries of their π-stacked core units, directed by the side chains (Figure 3). This notion suggests an interesting possibility that, without attaching electron-withdrawing or -donating groups to the electroactive core, both n- and p-type organic semiconductors are available from single π-conjugated motifs. In relation to this possibility, Brédas and co-workers reported in 2002 a theoretical prediction[15a] that assembled π-conjugated motifs possibly switch their preference for carrier species by changing the π-stacking geometry.[15] However, clear experimental supports have not been provided so far.

In conclusion, we demonstrated that the copper complex of a triply fused porphyrin dimer, when differently decorated at its periphery with appropriate side chains, can afford both n- and p-type liquid crystalline semiconductors (**P≡P$_{hetero}$** and **P≡P$_{homo}$**, respectively), where the side chains employed hardly change the intrinsic π-electronic properties but change the stacking geometry of the core. Although effects of assembly-directing side chains on charge-carrier mobilities have been recognized for several LC semiconductors,[16] nearly perfect switching of carrier species, as demonstrated for **P≡P$_{hetero}$** and **P≡P$_{homo}$**, is unprecedented. This finding is quite encouraging for diversification of organic semiconductors from limited available structural motifs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Details of synthesis and characterization of fused metalloporphyrin derivatives, MALDI−TOF mass and NMR spectra, X-ray diffraction patterns, electronic absorption spectra, time-of-flight data, and spectral simulation. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
aida@macro.t.u-tokyo.ac.jp

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