# Preparation, Crystal Structure, and Solid-state Fluorescence of a $CH_2Cl_2$-solvated Crystal of 6,13-Bis(*t*-butylphenyl)-2,3,9,10-tetrapropoxypentacene

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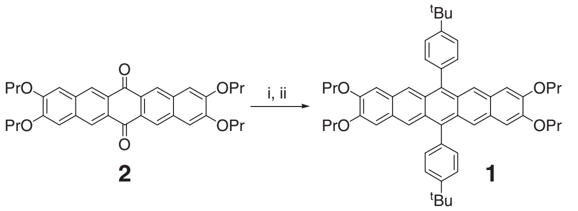
Slow evaporation of 6,13-bis(*t*-butylphenyl)-2,3,9,10-tetrapropoxypentacene in $CH_2Cl_2$ solution in the dark, yielded $CH_2Cl_2$-solvated single crystals easily. The crystals were characterized by X-ray analysis and solid-state fluorescence.

Linear oligoacenes have been studied widely as potential organic semiconducting materials for organic thin film transistors (OTFTs), organic light-emitting diodes (OLEDs), and photovoltaic cells.[1] In particular, pentacene derivatives have been intensively investigated because they exhibit high hole charge carrier mobility and a strong red emission.[2] The electronic and optical properties, solubility in organic solvents, and molecular arrangement in the solid state can easily be tuned by structural modification of substituents on the backbone. In an effort to tailor these properties, an increasing number of new pentacenes have been described.[3] Pentacenes that are stable in air and soluble in a variety of organic solvents have been pursued because of their processability and low cost involved in the development of applications. To that end, we prepared a new 6,13-diaryl-2,3,9,10-tetraalkoxypentacene **1**. This compound exhibited a unique behavior; on slow evaporation only from $CH_2Cl_2$ solution, $CH_2Cl_2$-solvated single crystals can easily be formed. We report here the preparation, crystal structure, and the solid-state fluorescence of **1**·$CH_2Cl_2$.

In order to obtain **1**, we applied a general preparative protocol,[4] namely addition of 4-(*t*-butyl)phenyllithium to 2,3,9,10-tetrapropoxy-6,13-pentacenequinone (**2**) and subsequent reduction as shown in Scheme 1.[5] We also succeeded in obtaining the other 6,13-diphenyl derivatives (e.g., phenyl and 2,6-dimethylphenyl) using this method. Pentacene **1** was a red-violet solid that showed relatively high air-stability and was soluble in common organic solvents such as $CHCl_3$ and toluene. The solutions were unstable in the presence of both light and air. Slow evaporation of $CH_2Cl_2$ solutions at room temperature in the dark yielded good quality single crystals. These crystals effloresced within hours of standing in air, turning into powder subsequently. This observation suggests that the single crystals we prepared can hold and release $CH_2Cl_2$. Using organic solvents other than $CH_2Cl_2$ led to powder formation exclusively. Consequently, we could not produce single crystals consisting only of **1**. Further, 6,13-diphenyl derivatives except **1** contained *t*-butyl groups that did not form the solvated crystals.



**Scheme 1.** Reagents and conditions: (i) *t*-$BuC_6H_4Li$, THF, −78 °C to rt, 62%; (ii) $SnCl_2$, AcOH–dioxane, 50 °C, 80%.

In order to examine the reason for using $CH_2Cl_2$ leading to the formation of single crystals, X-ray structural analysis was performed at −100 °C to clarify whether the single crystal crystallized was **1**·$CH_2Cl_2$.[5,6] Though there was one disordered set of propoxy groups, unambiguous structural information was obtained (Figure 1). Molecule **1** has a crystallographic center of symmetry, and half of the unit is asymmetric. The pentacene framework is almost planar and the peripheral benzene rings are almost perpendicular to the pentacene moiety. The dihedral angle between the planes of benzene and pentacene is 73.15(6)°. The carbon atom of the $CH_2Cl_2$ solvate is located at a short distance (3.327 Å) above the pentacene plane. The crystal packing of the pentacene backbone displayed a slipped-parallel arrangement constructed by the stacking of molecular sheets, although $\pi$-overlapping is absent because of the existence of the solvate. Within the molecular sheet, a $CH_2Cl_2$ molecule is surrounded by

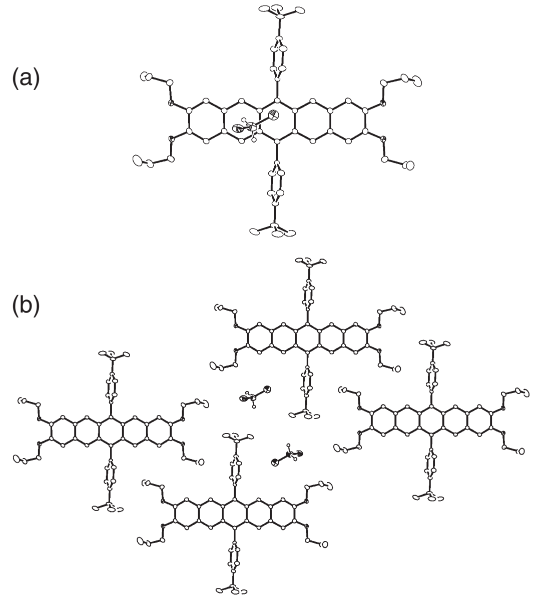


**Figure 1.** Crystal structures of **1**·$CH_2Cl_2$; (a) top view and (b) view normal to a molecular sheet.

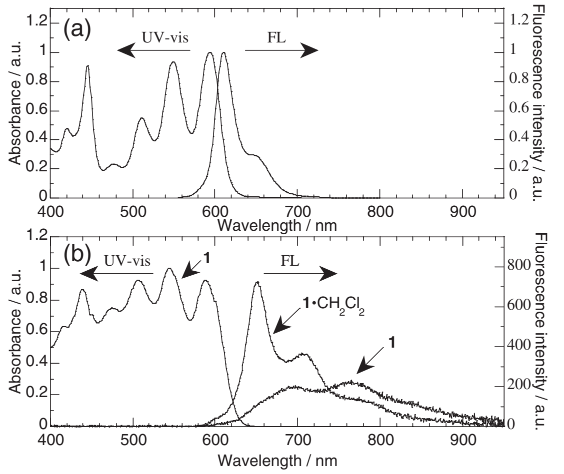


**Figure 2.** (a) UV–vis absorption and fluorescence spectra of **1** in $CH_2Cl_2$ and (b) Kubelka–Munk spectrum of **1** in diluted pellet, and fluorescence spectra of **1** in powder form and $\mathbf{1}\cdot CH_2Cl_2$ in crystalline form.

two *t*-butylphenyl and propoxy groups each, and a pentacene backbone (Figure 1b). The presence of *t*-butyl groups may be responsible for the formation of the solvated crystal. It can be assumed reasonably that the size and configuration of $CH_2Cl_2$ matched fortuitously with the vacant position in the molecular packing. Thus, the solvate molecule plays an indispensable role as a pillar in stabilizing the crystalline structure.

UV–vis absorption and fluorescence spectra of **1** in a dilute $CH_2Cl_2$ solution were measured (Figure 2a). The former shows a structured band with peaks at 511, 549, and 594 nm. The latter is slightly structured with the fluorescence maximum of 610 nm,[5] which represents a relatively small Stokes shift of 16 nm. Solid-state absorption (Kubelka–Munk) and fluorescence spectra of **1** were also measured (Figure 2b).[5,7] In the absorption spectrum of **1** in diluted pellet, all the major peaks appear at almost the same positions of the corresponding peaks of **1** in solution ($\lambda_{max} =$ 507, 545, and 589 nm). The fluorescence spectrum of $\mathbf{1}\cdot CH_2Cl_2$ in crystalline form is red-shifted by 41 nm with respect to that in the solution, whereas the fluorescence spectrum of **1** in the powder form shows more drastic change, i.e., the band at 651 nm found in $\mathbf{1}\cdot CH_2Cl_2$ disappears and the overall spectrum is further red-shifted and broadened. Along with these changes, the fluorescence quantum yield ($\Phi$) decreases in solid state. In fact, $\Phi$ of **1** in the solution and $\mathbf{1}\cdot CH_2Cl_2$ in crystalline form were 0.61 and 0.03, respectively, and $\Phi$ of **1** in powder form was too low to be measured ($\Phi < 0.01$).[5,8] It is reasonable to consider that the lower $\Phi$ values in the solid state results from concentration quenching,[9] efficient energy transfer into quench sites, and intermolecular interaction. In disordered systems, molecules form various packing structures without long-range order, and in many cases they exhibit absorption spectrum similar to that in the solution.[10] On the other hand, solid-state fluorescence may be dominated by some interacting molecules with lower energy (e.g. dimers), which are often contained in the disordered samples. A characteristic feature of solid-state fluorescence is red-shifted, the spectrum is broadened owing to intermolecular interaction, and nuclear displacement occurs in the excited state.[11] The fluorescence of **1** in powder form can be attributed to such interacting molecules. The ordered packing structure and solvated $CH_2Cl_2$ molecules in the crystals of $\mathbf{1}\cdot CH_2Cl_2$ are considered to weaken the intermolecular interaction and prohibit large nuclear displacement, resulting in a fluorescence spectrum rather similar to that in solution.

In conclusion, we found that **1** can easily make single crystals consisting of $\mathbf{1}\cdot CH_2Cl_2$ on slow evaporation from $CH_2Cl_2$ solution. Crystal packing of $\mathbf{1}\cdot CH_2Cl_2$ was confirmed by X-ray analysis. The fluorescence spectrum of $\mathbf{1}\cdot CH_2Cl_2$ was drastically different from that of **1** in powder form.

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5 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

6 Crystallographic details have been deposited with Cambridge Data Centre as no. CCDC-711919. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

7 It was impossible to measure the absorption spectra of $\mathbf{1}\cdot CH_2Cl_2$ in crystalline form technologically.

8 The lower $\Phi$ of **1** in powder form is responsible for the poor signal-to-noise ratio in the fluorescence spectrum in Figure 2b.

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