

New Biphenyl Derivative with Planar Phenyl–Phenyl Conformation in Crystal at Room Temperature Exhibits Highly Efficient UV Light-Emitting

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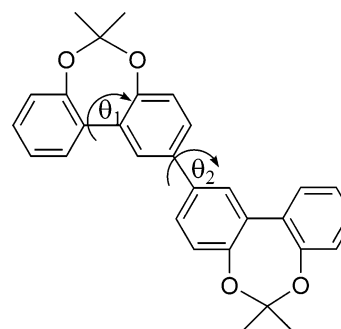
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The novel biphenyl derivative **1**, which has planar conformation in crystal at room temperature, is synthesized and investigated by X-ray diffraction. A hydrogen-bonding network, which may be the driving force for the formation of planar conformation, is observed in the crystal of **1**. **1** exhibits a strong UV-fluorescent emission in the solid state at room temperature.

The compounds with an aromatic–aromatic bond and their derivatives with extended structures (oligomers and polymers) have received considerable interest owing to their intriguing structural motifs and unique electroconductive, nonlinear optical, and luminescence properties.^{1–3} The inter-ring twisted angles in these compounds are widely studied because changes in the conformations of the conjugated molecules affect the optical and electronic properties significantly.⁴ For example, the bathochromic shift of the absorption and emission maximum in the conjugated polymer in the solid compared with that in solution may be corresponding to the conformational transition of conjugated backbone from twisting in solution to more planar in the solid state.⁵ The intermolecular interactions in the solid state may favor the coplanar arrangements of aromatic rings in the polymer chain and may be responsible for the observed conjugation enhancement. Therefore, the evaluating of the nature and driving force of conformational changes was very significant to design new functional materials. Biphenyl and its derivatives as model compounds have been paid more attention to their conformations. Most of the biphenyl derivatives showed the twisting conformation in their gas phase or solution, while in crystal, few of them have planar or nearly planar conformations at room temperature.^{6–8} The key factor determining the conformation changes in crystal is that the conjugation energy plus the crystal-packing energy is large enough to restrain the steric repulsion of ortho hydrogen atoms.⁹ In this paper, we designed and synthesized a new biphenyl derivative (structure shown in Chart 1), comprising of alternating rotation-limited (θ_1) and rotation-permitted (θ_2) phenylene–phenylene bonds in structure. Here we report its crystal structure and luminescence properties.

The biphenyl derivative **1** is a dimer of 6,6-dimethyl-dibenzo-[d,f][1,3]dioxepin, which was synthesized from the Ni(0)-catalyzed coupling reaction of 2-bromo-6,6'-dimethyl-dibenzo-[d,f][1,3]dioxepin.^{10,11} The compound **1** was crystallized from ethanol as a colorless block crystal. On the basis of a detailed

CHART 1: Molecular Structure of Compound **1**



analysis of IR, ¹H NMR, elemental analyses, and mass spectra, the structure was found to be consistent with structure **1**. It was further unequivocally confirmed by a single-crystal X-ray diffraction study.

A noteworthy feature of this molecule is its planar conformation (a torsion angle $\theta_2 = 0^\circ$) in crystal (Figure 1a), which is a large deviation from $\sim 51.9^\circ$ obtained from energy minimization calculations for **1** in the gas phase. In triclinic crystals of **1**, there are two molecules in the unit cell with space group *P*2-(1)/*c*. From the analysis of molecular packing in the crystal (Figure 1b), the face-to-face π – π interactions, which are thought as one of driving forces for decreased torsion angles in biphenyl, are not found (interplanar distance between parallel biphenyl plane is 7.32 Å). However, a weak hydrogen bond is found between the bridged oxygen atom with two hydrogen atoms on the 2,2' position of central biphenyl of **1**. The distances between the bridged oxygen atom with two hydrogen atoms on the 2,2' position of central biphenyl (O···H) are 2.620 and 2.828 Å, and the angles of O···H–C are 130 and 142°, respectively. The distance (between the hydrogen and oxygen atoms) and the angle (O···H–C) were consistent with weak hydrogen bonding by a previous report.^{12,13} Each two ortho hydrogens in both sides of central biphenyl can interact with oxygen in neighboring molecules leading to the formation of a hydrogen bonding

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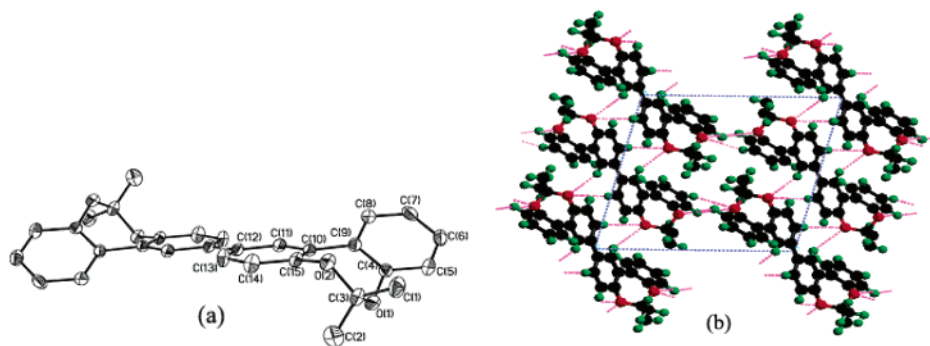


Figure 1. (a) ORTEP drawing of **1**. The ellipsoid probability is 25%. (b) Packing arrangement of **1**, viewed down the *a* axis. The atoms in the molecule and hydrogen bond between the molecules are colored as follows: carbon (black); oxygen (red); hydrogen (green); hydrogen bond (purple line).

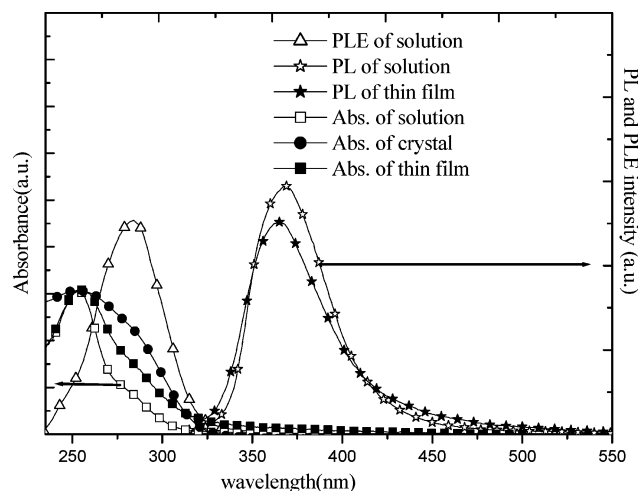


Figure 2. Absorption PL and PLE spectra of **1** in CHCl_3 and film. The absorption spectra of crystal samples were measured by diffuse reflection technology. PL was obtained as excitation at 300 nm, and PLE was obtained as emission at 370 nm.

network in crystal. This leads us to assign that the formation of such a network of hydrogen-bonding interactions plus crystal-packing forces in crystal is responsible for the planar conformation of **1**. It is reasonable that the repulsion between the two ortho hydrogen atoms can be overcome due to the formation of hydrogen bonding which increases the distance of the ortho hydrogen. Furthermore, the spatial configuration of **1** with the minimum potential energy was optimized via molecular mechanics simulations.¹⁴ It is demonstrated that a planar conformation is formed as present of $\text{O}\cdots\text{H}$ bond in the case of **1** crystal structure, while an isolated **1** molecule showed twisted conformation (a twist angle of about 51.9°).

Figure 2 showed UV-vis, photoluminescence (PL), and photoluminescence excitation (PLE) spectra in solution and a vacuum deposition film. The absorption spectra of diffuse reflection in crystal powder also showed in Figure 2. The major absorption bands were observed in diluted solution at 253 nm with a weak shoulder at 284 nm. Changing from solution to film state and from thin film to crystal powder does not change the position of the absorption band, but the intensity of the long-wavelength absorption band increases, indicating an increase in conjugation or an increase in the amount of molecules with the planar biphenyl conformation as **1** in solid. It was further unequivocally confirmed by simulated absorption spectra for different conformation. Spectral simulation demonstrated a clear increase in intensity of low-energy absorption band as **1** with conformation of $\theta_2 = 0^\circ$ as compared with $\theta_2 = 37.4^\circ$. The PL excitation spectrum shows a maximum at 284 nm in solution

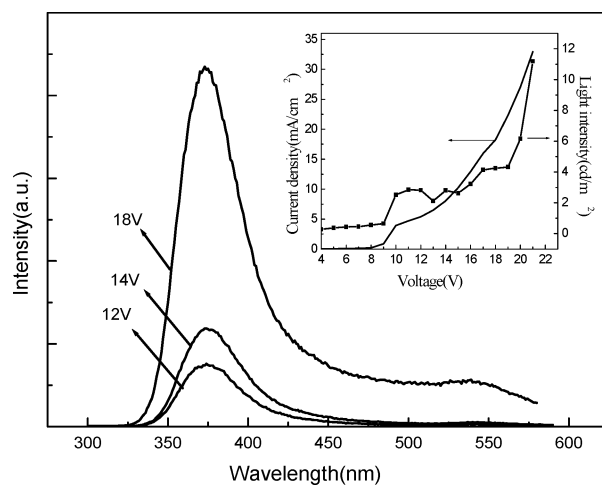


Figure 3. The EL spectra of the ITO/PDOT(60 nm)/**1**(50 nm)/Ba/Al device at driving voltages of 12, 14, and 18 V, respectively. Insert shows the current density (*I*)–voltage (*V*) and luminance (*L*)–voltage (*V*) characteristics of the device.

and film, indicating that long-wavelength absorption plays a main role in PL. It means that the planar biphenyl is the emitting center. When excited by 300-nm light, **1** shows strong UV emission, especially in film (solution, $\lambda_{\text{max}} = 369$ nm, $\Phi = 12\%$; solid, $\lambda_{\text{max}} = 363$ nm, $\Phi = 86\%$). The obvious increase in fluorescence efficiency of **1** from solution to solid can be attributed to the increase in the amount of the emitting center.

The monolayer organic light-emitting device (OLED) with the structure of ITO (indium tin oxide)/PDOT/**1**/Ba/Al was fabricated by thermal deposition in a vacuum chamber. The spectrum of EL showed the maximal emissive peak at 372 nm, which is consistent with the PL spectrum. The devices of compound **1** have a turn-on voltage at 9 V. The brightness of this UV-emitting device cannot be measured due to the spectral limitation of the luminance detector; however as estimation from the spectra tail that extended to visible spectral region, the maximum luminance is about 11 cd/m^2 and efficiency is about 0.07 cd/A (0.02 lm/W). Though the brightness and efficiency of this UV light-emitting device is lower than that of reported organic visible light-emitting devices and inorganic UV light-emitting devices, by our knowledge, it is the first neat organic device emitting UV light at room temperature.¹⁵ Because of the very high excitation energy of **1**, an attempt to improve the device efficiency by multilayer device structure is unsuccessful; a combination of **1** with hole-transporting layer material NPB¹⁶ or electron-transporting layer material Alq_3 ¹⁷ showed emission from NPB and Alq, respectively. In this way, new suited materials for constructing the multilayer UV light-emitting

device need to develop in future. In conclusion, the biphenyl derivative having intermolecular hydrogen bonding showed a coplanar conformation in crystal and exhibited strong fluorescence at the UV spectral region. Preliminary device experiments demonstrated the ability of this compound as the active layer for a UV light-emitting device at room temperature, which make it an excellent candidate for potential photo- and electroactive materials.

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Supporting Information Available: General experimental procedure, synthesis, characterization, crystal structure determination, and calculation of molecular simulation of compound **1** and characterization of the OLED device. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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