Effective Second-Order Nonlinear Optical Coefficient of a Novel Transparent Material: *N,N*-Diphenyl-8-[2-(4-pyridyl)ethenyl]dibenzofuran-2-ylamine

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(Received July 19, 2001; CL-010675)

N,N-Diphenyl-8-[2-(4-pyridyl)ethenyl]dibenzofuran-2-ylamine (**1**) has been synthesized and its second-order nonlinear optical coefficient has been examined by means of Second Harmonic Wave Generated with the Evanescent Wave (SHEW) method. As a result, **1** has been found to exhibit an effective *d* coefficient 3.0 times as large as that of urea. The cutoff wavelength of the compound was estimated to be 370 nm.

To date, a large number of organic materials which exhibit second-order optical nonlinearity have been reported.[1,2] It is well known for organic materials that the large delocalization of the π-electrons induces cooperative effects and produces large nonlinear optical (NLO) responses.[2] Therefore, in order to enhance the intramolecular charge-transfer, most of the molecules developed as nonlinear optical materials are equipped with strong donor and /or acceptor substituents such as nitro, amino, halo, cyano, hydroxy groups and so forth. Thus, these materials have a strong absorption band at the visible wavelength region in most cases. However, for practical application, the existence of an absorption band at fundamental or harmonic wavelength causes several problems. Therefore, a material which has a short cutoff wavelength and a moderately large molecular hyperpolarizability (β) is needed. Taking a variety of organic materials into consideration, there should be another molecular species which exhibit such properties.

In this study, we have attempted to find such a novel molecular species. Second-order optical nonlinearity of a crystalline sample is observed only when the component molecules are crystallized in a noncentrosymmetric space group. However, control of crystal structure is very difficult. As we[3,4] and another group[5] have already reported, bent-shaped molecules tend to crystallize in a noncentrosymmetric space group with anomalously high probability, and that some of them are promising and applicable second harmonic generation (SHG) crystals. Thus, we have newly designed a bent-shaped molecule which is expected to have a short cutoff wavelength. Namely, 2,8-disubstituted dibenzofran derivatives were synthesized. As a result, it is found that the *N,N*-diphenyl-8-[2-(4-pyridyl)ethenyl]dibenzofuran-2-ylamine (**1**) (see Figure 1.) exhibits a moderately large second-order NLO coefficient.

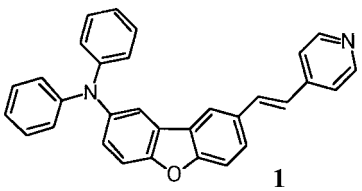

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Figure 1. Chemical formula of *N,N*-diphenyl-8-[2-(4-pyridyl)ethenyl]dibenzofuran-2-ylamine (**1**).

Compound **1** was synthesized as follows. 2-Diphenylamino-8-bromodibenzofuran was obtained as colorless crystals in a 20% yield by palladium-catalyzed monosubstitution of 2,8-dibromodibenzofuran with lithium salt of dipheylamine.[6] Compound **1** was obtained as colorless crystals (mp 152 °C) in a 49% yield by palladium-catalyzed Heck reaction of 2-diphenylamino-8-bromodibebzofuran with 4-vinylpyridine.

The NLO coefficients were evaluated by means of the Second-Harmonic Wave Generated with the Evanescent Wave (SHEW) method.[7] The Maker-Fringe method[8] is established as a reliable method to accurately estimate each component of the SHG tensor. However, it requires a high quality single crystal specimen of fair size with flat surfaces, as well as knowledge of wavelength dispersions of the refractive indices for analyzing the Maker-Fringe patterns. It is not always easy to grow such a large single crystal in case of an organic material. This situation has been hindering the estimation of an NLO coefficient of organic material. In contrast, the SHEW measurement does not require a large single crystal, which is actually the only means to estimate the largest tensor element of an NLO coefficient without using a single crystal. Therefore, this method is useful in evaluating an NLO coefficient of a given crystalline material. Thus, we have applied the SHEW method for the evaluation of the second-order NLO coefficient of **1**. A relative magnitude of effective NLO coefficient (d_{eff}) at 1.06 μm was determined by comparing the observed intensity of the SHEW signal with that of a reference sample of urea.[1] As a result, d_{eff} of **1** has been found to be as large as 3 pm/V.

As for cutoff wavelength, a rough estimation has been often made using the absorption spectrum for the solution, though this value is known to result in overestimation in some cases. The absorption spectrum of **1** taken in 10^{-5} M methanol solution is shown in Figure 2. Value at the axis of the abscissa, as extrapolat-

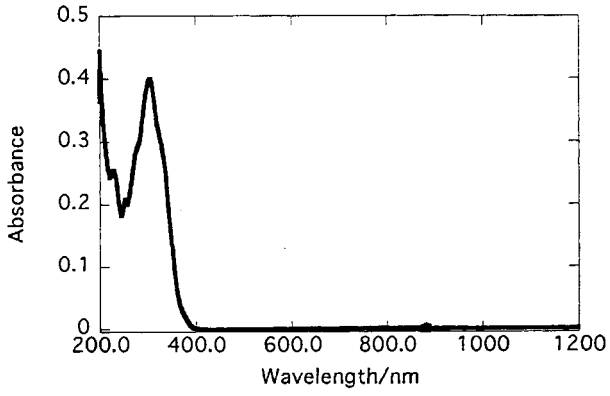

Figure 2. Absorption Spectra of **1** taken in 10^{-5} methanol solution.

Table 1. Comparison of the SHG characteristics between **1** and some well-known organic SHG crystals.

Characteristics	**1**	MHBA[a]	APDA[b]	5-NU[c]
Cutoff Wavelength / nm	370	370	384	410
NLO coefficient at 1.06 μm / pm/V	$d_{eff} = 3$	$d_{13} = 13$ $d_{11} = 9.8$	$d_{31} = 7$ $d_{33} = 50$	$d_{14} = 5.2$
Melting Point / °C	152	82	123	>300(decomp)
Reference	this work	9	10	11

[a]3-Methoxy-4-hydroxybenzaldehyde. [b] 8-(4-Acetylphenyl)-1,4-dioxa-8-azaspiro[4.5]decane. [c]5-Nitrouracil.

ed from the steepest tangent in the absorbance curve, is adopted as the cutoff wavelength. The value has been estimated to be 370 nm. As mentioned above, **1** is a colorless crystal. This fact indicates that the cutoff wavelength of **1** is shorter than at least 400 nm even in the crystalline state. The cutoff wavelengths of almost all SHG materials have been reported to be longer than 400 nm.[1] Only a few compounds are known to have a cutoff wavelength shorter than 400 nm.[1] Therefore, it is natural to consider that **1** should be one of a valuable SHG material.

Here, let us compare the d_{eff} of **1** with d_{ij} of some of well-known organic SHG materials having the similar cutoff wavelength. As shown in Table 1, the d_{eff} observed for **1** by the SHEW method appears to be smaller than d_{ij} of well-known materials by the Maker-Fringe method. However, we notice that the largest tensor element of 8-(4-acetylphenyl)-1,4-dioxa-8-azaspiro[4.5]decane (APDA) is the diagonal tensor element. As for the practical application, the phase-matching characteristic is very crucial. The phase-matched efficiency is mainly dominated not by diagonal tensor element of d_{ij} but by off-diagonal one. Therefore, in order to obtain efficient SHG output, the SHG crystal must have a large off-diagonal tensor element. According to our preliminary experiment, **1** is phase-matchable. In addition, it is reported that an SHG crystal composed of a bent-shaped molecule tends to have a larger off-diagonal tensor element than the diagonal ones.[3,12] Therefore, it is natural to consider that the d_{eff} of **1** arises from an off-diagonal tensor element. The off-diagonal values observed for APDA and 5-nitrouracil (5-NU) are not so larger than d_{eff} of **1**. In addition, the cutoff wavelength of **1** is shorter than those of APDA and 5-NU. Although the cutoff wavelength of 3-methoxy-4-hydroxybenzaldehyde (MHBA) is the same with that of **1** and the off-diagonal tensor element of the NLO coefficient of MHBA is larger than the d_{eff} of **1**, the melting point of **1** is higher than that of MHBA. Generally speaking, the low melting temperature often restricts the range of applications.[11] Thus, 5-NU, which exhibits very high melting point, is still one of the most promising SHG materials, though the NLO coefficient is not so large.[11] Consequently, it is concluded that **1** should be one of promising candidates for SHG material having a cutoff wavelength of 300's nm.

In conclusion, we have found that **1** exhibits a moderately large NLO coefficient of 3 pm/V and has a short cutoff wavelength of 370 nm. This fact indicates that the 2,8-disubstituted dibenzofuran frame has a potential ability to be a promising SHG material. Therefore, there should be a possibility that a more promising 2,8-disubstituted dibenzofran derivative than **1** can be designed by modifying the terminal substituent. The study is now in progress.

References and Notes

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