

# Revealing bipolar charge-transport property of 4,4'-N,N'-dicarbazolylbiphenyl (CBP) by quantum chemical calculations

Tomonori Yamada<sup>a</sup>, Furitsu Suzuki<sup>a</sup>, Atsushi Goto<sup>a</sup>, Tohru Sato<sup>b,c</sup>, Kazuyoshi Tanaka<sup>b</sup>, Hironori Kaji<sup>a,\*</sup>

<sup>a</sup> Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

<sup>b</sup> Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

<sup>c</sup> Fukui Institute for Fundamental Chemistry, Kyoto University, Takano-Nishihiraki-cho 34-4, Sakyo-ku, Kyoto 606-8103, Japan

## ARTICLE INFO

### Article history:

Received 8 August 2010

Received in revised form 18 October 2010

Accepted 31 October 2010

Available online 12 November 2010

### Keywords:

Organic LED

Marcus theory

Charge transfer integral

Reorganization energy

Quantum chemical calculation

## ABSTRACT

4,4'-N,N'-Dicarbazolylbiphenyl (CBP) has both the hole- and electron-transport ability, that is, bipolar charge-transport property, and has been widely used for organic light-emitting diodes (OLEDs). In this study, we explain the bipolar charge-transport property of CBP by quantum chemical calculations for the crystal. Both the reorganization energies and the charge transfer integrals were investigated, and charge-transfer rate constants were calculated based on Marcus theory. The hole- and electron-transfer rate constants thus calculated were found to be similar in magnitude. This is in sharp contrast with the case of a structurally similar but a poor electron-transport material, N,N'-diphenyl-N,N'-di(*m*-tolyl)benzidine (TPD), for which the hole-transfer rate constants were calculated to be much larger than the electron-transfer rate constants. From the detailed analysis of the charge transfer integrals for CBP, it was found that holes transfer through all the segments of the molecules, using the delocalized HOMO over the whole molecule as in the case of TPD. On the other hand, electrons transfer advantageously through the delocalized LUMO on the carbazole moieties of CBP, which have close intermolecular contacts. The LUMO of TPD localizes on the central biphenylene moiety, resulting in small electron transfer integrals. The results clearly show the difference of the electron-transport property between CBP and TPD.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

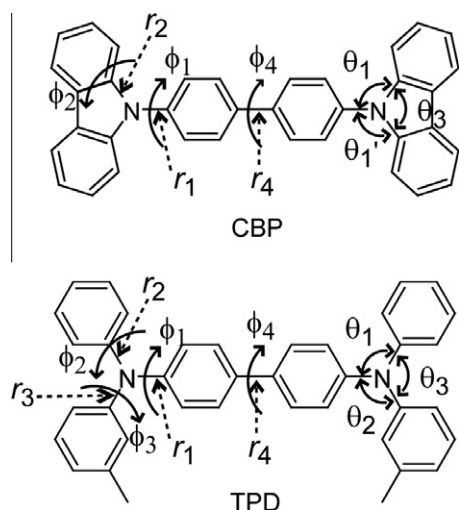
Organic light-emitting diodes (OLEDs) are promising devices for flat or flexible displays, and lighting equipments [1,2]. Fig. 1 shows widely known charge-transport materials for OLEDs, 4,4'-N,N'-dicarbazolylbiphenyl (CBP) [3–10] and N,N'-diphenyl-N,N'-di(*m*-tolyl)benzidine (TPD) [2,11–16]. The chemical structures of CBP and TPD are similar to each other, while the charge-transport properties are not. For CBP, both the hole and electron mobilities are on the order of  $10^{-3}$  cm<sup>2</sup>/Vs [7,8]. Conforming to the preceding studies [5,7–10], we should like to call CBP

as a 'bipolar' material on the basis of the comparable hole and electron mobilities. The latter, TPD, shows a similar hole-transport property with the mobility of  $\sim 10^{-3}$  cm<sup>2</sup>/Vs; however, the electron mobility is inferior,  $< 10^{-7}$  cm<sup>2</sup>/Vs [14–16]. Understanding the origins of the different charge-transport properties between CBP and TPD is of importance not only for fundamental science but also for molecular designs with excellent performance.

Charge transports in organic materials have often been discussed based on Marcus theory [17,18], which describes the charge-transfer rate constant,  $k_{CT}$ , as Eq. (1).

$$k_{CT} = \frac{4\pi^2}{h} H_{AB}^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{\lambda}{4k_B T}\right) \quad (1)$$

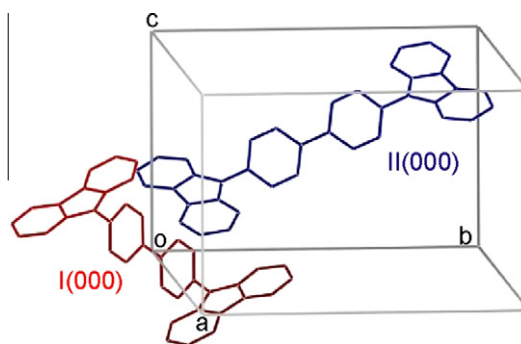
\* Corresponding author. Tel.: +81 774 38 3149; fax: +81 774 38 3148.  
E-mail address: [kaji@scl.kyoto-u.ac.jp](mailto:kaji@scl.kyoto-u.ac.jp) (H. Kaji).



**Fig. 1.** The chemical structures of CBP and TPD. The  $\theta$ ,  $\phi$ , and  $r$  represent bond angles, torsion angles, and bond lengths, respectively.

Here,  $\lambda$  is the reorganization energy, and  $H_{AB}$  is the charge transfer integral between the relevant two molecules. The temperature,  $T$ , is fixed at 300 K throughout this paper. The  $h$  and  $k_B$  are the Planck and Boltzmann constants, respectively. In some studies, for example, Refs. [19] and [20], reorganization energies were calculated to account for the charge-transport properties. The charge transfer integrals were assumed to be similar in these studies. The attempts were partly successful for the qualitative description of the charge-transport properties. However, it has been found that some experimental results cannot be explained by the simple consideration. For tris(8-hydroxyquinoline) aluminum(III) ( $\text{Alq}_3$ ), for example, the difference between the hole- and electron-transport properties could not be explained by the consideration only of the reorganization energies. The charge transfer integrals were found to be a key factor [21].

Recently, we found that the hole transfer integrals in TPD crystals are several times larger than the electron transfer integrals [22]. The HOMO of TPD spreads over the molecule. Large intermolecular overlaps can be formed between the phenyl and/or tolyl rings, which have close



**Fig. 2.** The unit cell of CBP crystal and representations of molecules I and II. The cell parameters are as follows;  $a = 8.01 \text{ \AA}$ ,  $b = 16.01 \text{ \AA}$ ,  $c = 10.24 \text{ \AA}$ ,  $\alpha = \gamma = 90.0^\circ$ , and  $\beta = 110.2^\circ$ .

intermolecular contacts in the crystals. In contrast, the LUMO of TPD is localized on the central biphenylene moiety, which results in small intermolecular overlaps (that is, small electron transfer integrals). Owing to both the small reorganization energies and the large charge transfer integrals for the hole transfers, the hole-transfer rate constants were calculated to be more than two orders of magnitude larger than the electron-transfer rate constants. In addition, there are effective hole-transport paths consisting of consecutive molecular pairs with large hole-transfer rate constants [22]. The results show the favorable hole-transport property of TPD.

On the other hand, the origins of the bipolar charge-transport property of CBP have been unclear, despite the practical importance as a host material of emitting layers in OLEDs. In this paper, we analyze the charge-transport property of CBP in the crystal as in the case of TPD. The reorganization energies and the charge transfer integrals are compared with those for TPD. The results explain the difference of charge-transport properties between CBP and TPD.

## 2. Computation

The structural optimizations were performed for neutral, cationic, and anionic CBP molecules by DFT method using the B3LYP functional [23–25] and the 6-31G(d) basis

**Table 1**

Structural parameters of a CBP molecule in the crystal, and those optimized by DFT method for the neutral, cationic, and anionic states. The parameters are defined in Fig. 1. As an initial structure for the optimizations, the crystalline structure was adopted. The parameters for the optimized TPD are also shown for comparison.

		Bond angle ( $^\circ$ )			Torsion angle ( $^\circ$ )				Bond length ( $\text{\AA}$ )			
		$\theta_1$	$\theta_2$	$\theta_3$	$\phi_1$	$\phi_2$	$\phi_3$	$\phi_4$	$r_1$	$r_2$	$r_3$	$r_4$
<b>CBP</b>												
Crystal <sup>a</sup>		$125 \pm 1$	–	108	$49 \pm 3$	$9 \pm 2$	–	0	1.42	$1.39 \pm 0.01$	–	1.49
Optimized	Neutral	126	–	108	53	2	–	0	1.42	1.40	–	1.49
	Cation	126	–	108	45	4	–	0	1.40	1.41	–	1.47
	Anion	126	–	108	70	1	–	0	1.43	1.39	–	1.44
<b>TPD</b>												
Optimized	Neutral	120	120	120	41	41	43	36	1.42	1.42	1.42	1.48
	Cation	121	121	118	26	49	49	21	1.39	1.43	1.43	1.46
	Anion	119	119	122	61	31	32	9	1.44	1.41	1.41	1.44

<sup>a</sup> The values are taken from Ref. [26].

Download English Version:

<https://daneshyari.com/en/article/1267741>

Download Persian Version:

<https://daneshyari.com/article/1267741>

[Daneshyari.com](https://daneshyari.com)