Design for Charge Transport Property of Positive-Charging -Type Single-Layer OPC Photoreceptor

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Abstract

This report presents a study of design for charge transport property of positive-charging-type single-layer OPC photoreceptor (PSLP) having highly photosensitivity and high photoresponse using an electrophotographic imaging system. Tow design objectives are demonstrated as follows. (1) In the PSLP which has dispersed p-type charge generation material, we confirmed that the existence of ETM is one of dominant factors for photosensitivity. (2) In the design for high-sensitive PSLP, it has revealed it is important to select the combination of HTM and ETM in consideration of dipole moments. In other words, in ternary solid solutions of phenylendiamine (PDA) as a hole transport material (HTM) and phenylnaphthquinone (PNQ) as an electron transport material (ETM) in bisphenol-Z type polycarbonate (PC-Z) as a binder resin, a significant increase in the electron mobility have been observed. The effect is attributed to the elimination of random dipolar field s due to static dipole moments of the carbonyl groups of the polycarbonate.

Introduction

Recently the color printers and color multi-functional peripherals have been increased in number rapidly. Therefore also in the electrophotographic photoreceptor, the demand of improvement of sensitivity, durability and resolution of image has been increased further. We have so far developed positive-charging-type single-layer OPC photoreceptor (PSLP).[1,2] PSLP has the advantage of excellent image quality compared with negative-charging-type dual-layer OPC photoreceptor in some respects.[3,4] Moreover, we are also promoting development of high durability technology. Consequently we have achieved the long-life OPC drum, high durability type PSLP, for the tandem color printers of the small size which guarantees printing of 200,000 sheets. On the other hand, improvement in photosensitivity of PSLP is also one of the important technical development items.

It is important for an improvement in the photo-sensitivity of a photoreceptor to understand the generation mechanism of the photosensitivity and the function of materials that are comprised of photoreceptor. Photo-induced discharge process in PSLP is shown in Figure 1. It has been divided into three primary processes, i.e., charge generation, charge injection and charge transportation. However the interaction between composition materials of PSLP cannot be disregarded, since there are predominant three materials, i.e., charge generation material (CGM), hole transport material (HTM), electron charge material (ETM), co-dispersed in a binder resin (Figure 2). Additionally it is necessary to take account of influence of electric field distribution, re-combination.[5] etc. Therefore, it is not only important to pursuit each high efficient materials which governs sensitivity in development of PSLP but to design the device in consideration of an interaction, a space electric charge and re-combination.

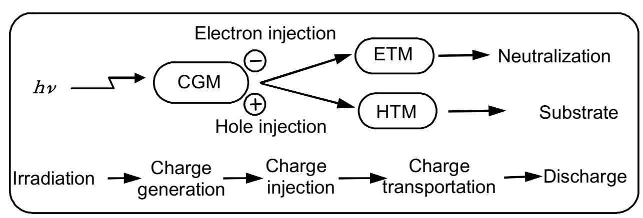

Figure 1. Photo-induced discharge process in a positive-charging-type single layer OPC.

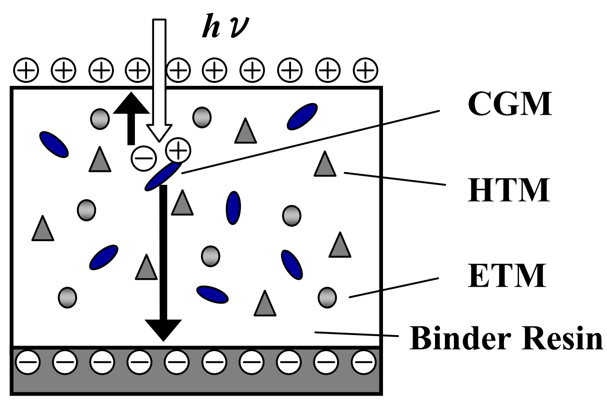

Figure 2. Cross section of a positive-charging-type single-layer OPC

This paper describes a study of the improvement in the photosensitivity of PSLP due to an interaction of charge transport property between HTM and ETM.

Experimental

The sample drums of PSLP for the electrophotographic property measurements were prepared by dispersing mixtures of CGM (1.5wt%), HTM (35wt%), ETM (17.5wt%) and bisphenol-Z type polycarbonate (PC-Z) as binder resin in tetrahydrofurane and then coating the resulting solutions on aluminum tubes using ring coater. x-form metal-free-phthalocyanine (x-H_2Pc) as CGM was used. These drums were dried in air 110°C for 60min. The thicknesses of dried photoreceptor layer on drums were about 30μm. Drum photoconductor evaluation apparatus (C30M, GENTEC) was utilized to measure electro-photographic properties of PSLP Drum. The molecular structures that were phenylendiamine (PDA), tetraphenyl-daiminobiphenyl (TPD) as HTM, naphthquinone (PNQ) and bisnaphthquinone (BNQ) as ETM, used in this study are shown in Figure 3.

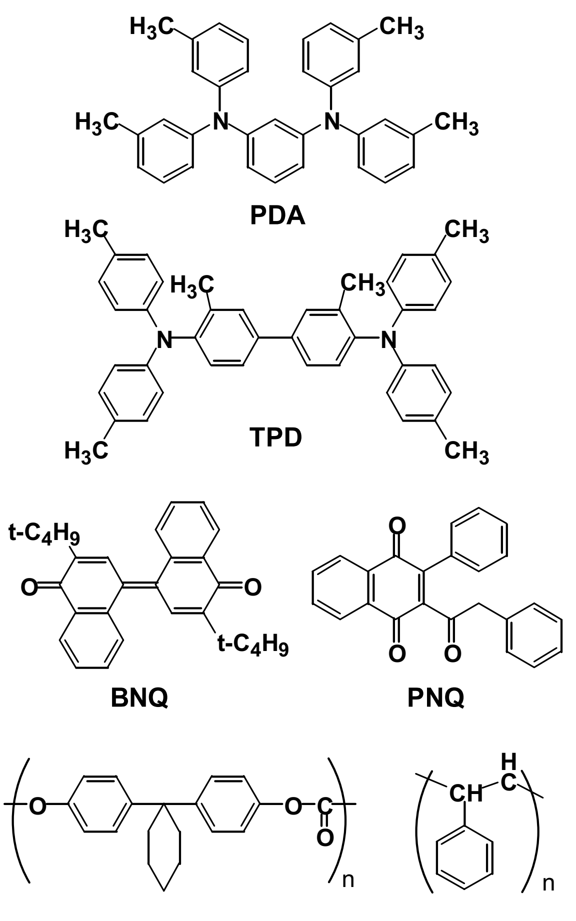

Figure 3. Molecular structures of HTM, ETM and binder resin.

The sample films for the drift mobility measurements were prepared by dissolving mixtures of 30wt% of HTM or ETM and 70wt% of binder resin in tetrahydrofurane and then coating the resulting solutions on aluminum sheets using wired bar. These films were dried in air 75°C for 30min. The thicknesses of dried films were between 5 and 10μm. Finally, a semitransparent gold electrode was vacuum-deposited on the free surface of coatings. Also in the case of co-dispersion films as HTM and ETM in a binder resin at various dopant compositions with a total dopant concentration of 50wt%, they were prepared by same procedure. Instead of PC-Z, polystylene (PS) was used as binder resin in order to elucidate the effect of host polymer.

The drift mobility measurements were performed by conventional time-of-flight (TOF) technique. By this method, the displacement of a sheet of charge carrier injected into the molecular doped layer is time resolved. Photoexcitation of photoemitting electrode was by pulse exposure of 337 nm radiation derived from a N_2 laser.

Results and Discussion

Electrophotographic Properties of PSLP

Electrophotographic properties of sample drums are shown in table 1. $E_{1/2}$ is half decay energy. VL is surface potential when 340 ms passes after exposure for 50ms by the light intensity of 20 μWcm^{-2}. Hole mobility of HTMs and electron mobility of ETMs used in sample drums are shown in table 2.

Table 1. Xerographic Properties of Single-Layer OPCs (Binder Resin : PC)

Sample	HTM	ETM	$E_{1/2}$ / μJcm^{-1}	VL / V
1	PDA	-	0.79	171
2	PDA	PNQ	0.84	155
3	PDA	BNQ	0.82	143
4	TPD	PNQ	0.79	142
5	TPD	BNQ	0.66	122

Table 2. Mobility of HTMs and ETMs in PC-Z

HTM	hole mobility $/cm^2V^{-1}s^{-1}$	ETM	electron mobility $/cm^2V^{-1}s^{-1}$
PDA	3.9×10^{-6}	PNQ	2.0×10^{-8}
TPD	5.9×10^{-6}	BNQ	4.3×10^{-7}

CTM concentration in PC-Z is 30wt%, F=5 x $10^5 Vcm^{-1}$

The VL of the drum samples 2-5 in which ETM exists exhibited lower value compared with sample 1 (only PDA) although there is slightly difference in value of $E_{1/2}$. While n-type CGM functions as electron transport manifolds by itself in PSLP,[1] ETM, which behave as an electron accepter and transporter, is required for PSLP used p-type CGM as x-H_2Pc. In other words, the existence of ETM is one of dominant factors for photosensitivity.

From a relation with the mobility, photosensitivity is improved, so that the value of either HTM or ETM is high. Although the distance of electrons which move is short to hole, it exhibited certain sensitive also at a quite low mobility of PNQ. It is therefore expected that interactions exist, such as enhancing the photosensitivity by ETM.

Mobility of Co-Dispersion Film

Figure 4 shows the field dependence of electron mobility for the co-dispersion film of HTM and ETM in PC-Z. Although hole mobility seldom changes with the value of HTM only, a significant increase in the electron mobility is observed.

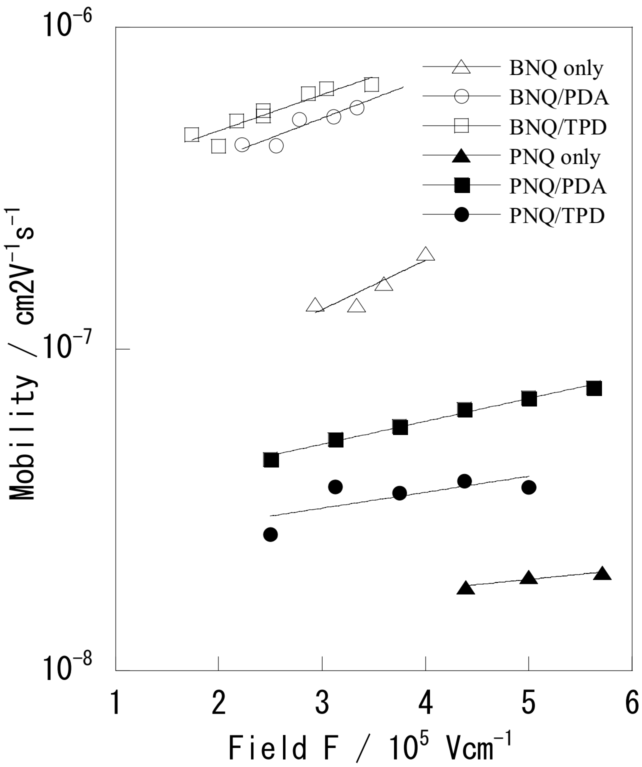

Figure 4. Field dependence of electron mobility in ternary solid solutions of HTMs (30wt%) and ETMs (30wt%) in PC-Z.

Yamaguchi and co-workers have studied hole transport properties of ternary solid solutions composed PDA and 3,5-dimethyl-3',5'-di-t-butyl-dipenoquinone (DQ) in PC-Z at various dopant compositions with a total dopant concentration of 50 wt%.[6] They concluded that the charge transportations of both hole and electron were functioned independently without the interaction like a decrease mobility due to donor-accepter CT-complex formation from results that mobility in co-dispersion film were agreement with them in dispersion film of mono-component in PC-Z. In order to confirm this disagreement, evaluations of a similar system was performed.

Mobility at Various Dopant Compositions

Electron and hole mobility in ternary solid solutions of PDA and PNQ in PC-Z at various dopnat compositions with a total concentration of 50 wt% are shown in Figure 5. There is little influence on a hole transport property by existence of ETM. In contrast to this, result shows that improvement of electron mobility over a range of every dopant composition in this measurement and the tendency which they increase as the concentration of PDA as HTM is higher. It is indicated clearly that the existence of HTM is important factor for electron transport phenomena in the co-dispersion film. Additionally it demonstrated that this improvement of electron mobility is one of predominant factor for high sensitivity of PSLP used p-type CGM.

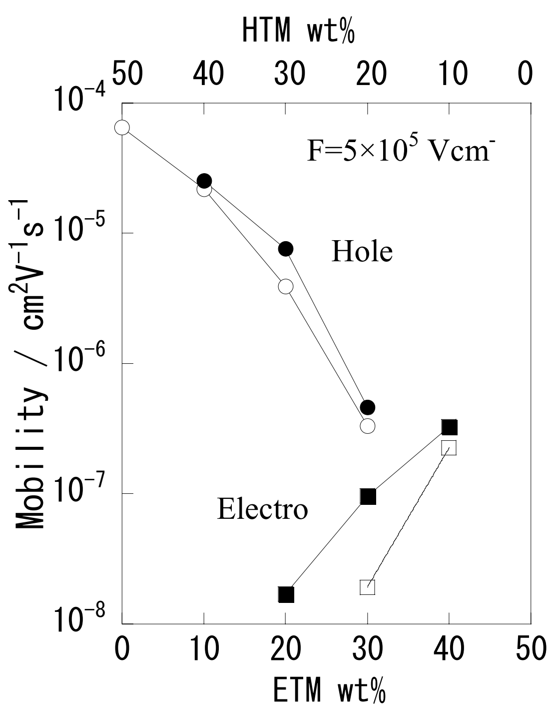

Figure 5. Electron and hole mobility in ternary solid solutions of PDA and PNQ in PC-Z at various dopant compositions with a total dopant concentration of 50wt%.○:hole mobility of PDA only, ●:hole mobility of PDA/PNQ, □:electron mobility of PNQ only, ■:electron mobility of PNQ/PDA.

The Effect of Binder Polymers

In order to confirm another factor of interaction by the host polymer, electron mobility of co-dispersion film in PS were measured. Figure 6 shows the field dependence of mobility. Consequently, it was observed further improvement of electron mobility replacing the PC-Z with PS. Boresenberger and co-worker have reported that a significant increase in the electron mobility of DQ doped in polymer is observed upon replacing the PC-Z with polystyrene (PS).[7] They have described this phenomena by a model based on disorder. It was argued that the increase in mobility in this case was due largely to the reduction in the energy width of the distribution of hopping sites which, in turn, was related to the elimination of random dipole fields due to static dipole moment associated with the carbonyl group in PC-Z. In tenary solid solution, since polarity of PDA as HTM is comparatively weak, it has reduced the influence due to a polar group of PC-Z.

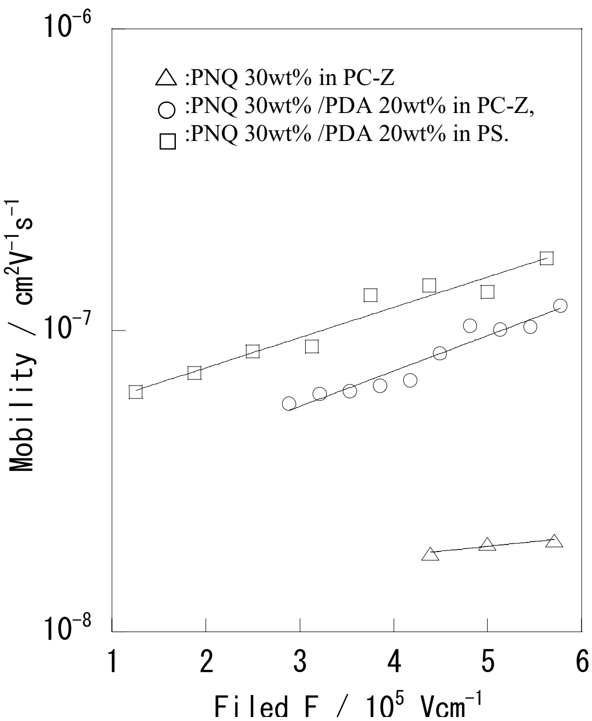

Figure 6. Field dependence of electron mobility in ternary solid solutions of PDA and PNQ in PS.

It is so far important for improvement in photosensitivity of PSLP to develop highly efficient materials i.e., CTMs have high mobility. However, the combination of HTM and ETM may be set to one of the design techniques of PSLP from the above results.

Conclusion

The following things were clarified about the characteristic of electric charge transportation material.

In the PSLP which has dispersed p-type CGM, we confirmed that the existence of ETM is one of dominant factors for photosensitivity.

In the design for high-sensitive photoreceptor, it has revealed it is important to select the combination of HTM and ETM in consideration of dipole moments.

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Biography

Eiichi Miyamoto received his B.S. degree in Chemistry from Kwansei Gakuin University at Nishinomiya in 1985. Since 1985 he has worked in the Photoreceptor Project Division of Mita Industrial Co. Ltd., (Now, Kyoceramita Corporation). His work has primarily focused on the development process, including the device design and materials for OPC photoreceptor. He is a member of the Imaging Society of Japan.