Diphenoquinone Derivatives and Their Applications as Charge Transport Material in Single-layered Organic Photoreceptor

Weimin Zhang, Ti Wu, Wenguang Wang and Jialing Pu; Lab. Printing & Packaging Material and Technology, Beijing Institute of Graphic Communication; No.25, Xinghua Beilu, Huangcun, Daxing, Beijing, China

Abstract

A series of diphenoquinone derivatives were synthesized and their molecular structures were confirmed with IR, NMR and EA. The diphenoquinone molecules were characterized by asymmetrical structures and found highly soluble in common organic solvents and polymers. They could be dissolved in polyesters, like PC (polycarbonate), Vylon200 (a polyester) and etc., at high concentrations above 40 wt%. The diphenoquinone derivatives were used as electron transport material (ETM) and incorporated together with a hole-transport material (HTM) and a charge generation material (CGM) into either PC or Vylon 200 to form a single-layered organic photoreceptor. Xerographic performances of the single-layered multi-components photoreceptor were systematically investigated. For the ETM, HTM and CGM doped single-layered photoreceptors, their photosensitivity was strongly dependent on ETM concentration. Half decay exposure dropped down sharply with increasing ETM concentration and reached minimum when ETM"s concentration was 10 wt% and then slightly increased at even higher ETM concentrations. When exposed at 780 nm, the lowest half decay exposures of positive- and negative-charging were 2.2μJ/cm^2 and 2.8μJ/cm^2, respectively. For the HTM or ETM and CGM doped single-layered photoreceptor, charge generation was localized in the surface of photoreceptor and the bulk of photoreceptor acted only as the space for charge transport when CGM's concentration was 15wt% or higher. This kind of single-layered photoreceptor had separated charge generation and transport functions and worked very much like a dual layered photoreceptor. Half decay exposure was found a decreasing function of CTM's concentration. The lowest half decay exposure under optimized conditions was 9.6μJ/cm^2 and 0.59μJ/cm^2 by using ETM's and HTM's at 780nm wavelength with excellent xerographic performances.

Keyword: Diphenoquinone derivatives, Asymmetrical structure, single-layered photoreceptor, Xerographic performance

Introduction

As a key element in organic photoreceptor, charge transport materials play an important role in xerographic imaging process. The capability of charge transport materials largely determines xerographic performance of organic photoreceptor. At present, there are various kinds of hole-transport materials (HTM) which have excellent hole-drift mobility and have been widely used in dual-layer negative-charging organic photoreceptor. The non-uniform distribution of the surface charge caused by corona charging is an important factor to influence imaging quality, and the negative charging wise is environment unfriendly. And that organic electron transport materials (ETM) currently have three problems, that is, (1) lack of molecular diversities and poor capability, (2) lower drift mobility and (3) poor compatibility with polymers. Poor compatibility makes the molecule hard to be doped into polymer at high concentrations (e.g. over 40 wt.%) [1-2], as required by most applications such as xerographic imaging device. For this, it is apparently justified to investigate new ETM which offers excellent properties. Positive changing dual-layer organic photoreceptors which exhibit excellent performance will be constructed. Diphenoquinone was believed to be a possible and promising candidate [3-4]. With its molecular structure, the two oxygen atoms, which are bridged by a large conjugated π electron system, act as strong electron affinitive/receiving moieties. Another attractive advantage of this molecule lies in the fact that it offers a number of active sites for chemical modification. This will allow electron affinitive and other important properties of the molecule to adjust independently. It has better solubility in organic solvent (such as chloroform and tetrahydrofuran) and better compatibility with polymers. Better compatibility with means that the molecule will be easily doped into polymers at a concentration exceeding 40 wt.%.

In this paper, a study was carried out on the synthesis of diphenoquinone, and the xerographic performances of photoreceptor which contains CGM, HTM and ETM. Excellent performances may be achieved.

Experimental

Diphenoquinone derivative preparation and its structural confirmation

Three compounds, ETM1, ETM2 and ETM3, were prepared in our laboratory [5-6] and used as ETMs, Their molecular structures were shown in Figure 1. Their structures were confirmed by using infrared spectrometer (FTIR-8400), ^{1}H NMR, ^{13}C NMR (FA-80A) and MS (AEI-MS50).

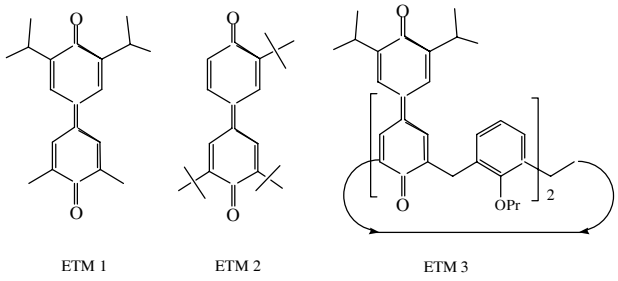

Figure 1. *Molecular structure of diphenoquinone derivatives*

Electron transport materials, 2,5-dimethyl-2',5'-diisopropyl diphenoquione (ETM1, red needle-like crystal, mp: 135.4-236.5 ^{o}C), 2,-2',5'-tri-tert-butyl diphenoquione (ETM2, mauve crystal mp: 133.5 ^{o}C) and a ring-structured diphenoquione derived from calix[4] (ETM3, red needle-like crystal, mp: not found before decomposition).

Preparation of Organic Photoreceptor

Y-TiOPc was used as charge generation material (CGM), Diphenoquinone derivative and TNF were used as the electron transport material (ETM) and the hole-transport material, Vylon200(a polyester) and polycarbonate were used as the polymer matrix and a 0.3 mm thick aluminum plate was used as the substrate. Y-TiOPc and Diphenoquinone derivative were prepared in our Lab. HTM, TNF, polycarbonate and Vylon200 were commercial product.

Under continuous agitation, binder polymer was completely dissolved in purified THF and then HTM and ETM were added, giving a transparent solution. Then, CGM was added and the solution was subjected to mechanical and supersonic agitations. The coating solution was applied to the substrate by using a modified dipping coater. The sample was dried in an open-air oven at 80 ^{o}C for 5 h and then kept in a dark room for at least one night before measurement was made. The final photoreceptor was about 15μm thick.

Measurement of Xerographic Performance

Xerographic properties were examined by using a home-made device named as EMS'93. A 400W xenon lamp was used as the exposure light and monochromatic radiation was obtained by passing the light through a monochromator. Light intensity was measured by using Gamma Scientific's Digital Radio/Photometor DR-1600.

Results and Discussion

Compatibility of ETMs with Polymer

Solubility of ETMs in organic solvents and their compatibility with polymers directly influence the properties of OPC devices. Here, chloroform and tetrahydrofuran were used as organic solvent to evaluate resolvable the solubility. Experimental results revealed that the maxium solubility of ETM1, ETM2 and ETM3 was over 40%, indicating that they have excellent solubility.

Xerographic Performance of tercomponent single-layered organic photoreceptor

Figure 2 is the sketch map of tercomponent single-layered organic photoreceptor. The photoreceptor has a thin-layered polymer matrix doped with charge generation material (CGM), electron transport material (ETM) and hole-transport material (HTM). Since the concentration of CGM was lower than 1.2 wt.%, the photoreceptor is virtually transparent. In this situation, charge generation takes place throughout the whole layer, and photogenerated electrons and holes drift in the same place. This builds separate channels for effective charge generation, electrons and holes transportation. Therefore, the photoreceptor was characterized with bipolarity charging, namely, positive charging and negative charging.

Figure 3 shows the relationship between half decay exposure and concentration of different ETMs. It was found that photosensitivity was strongly dependent on the ETM's concentration. Half decay exposure dropped down sharply with increasing ETM's concentration and reached the minimum value when ETM's concentration was 10 wt.% even if higher ETM's concentrations were employed. When ETM's concentration was over 20 wt.%, the half decay exposure tended to become stable.

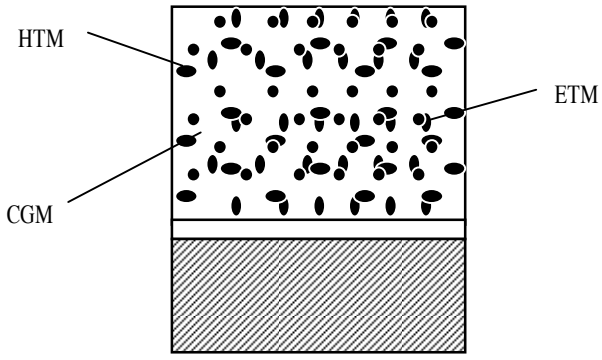

Figure 2. *The Structure of tercomponent single-layered organic photoreceptor*

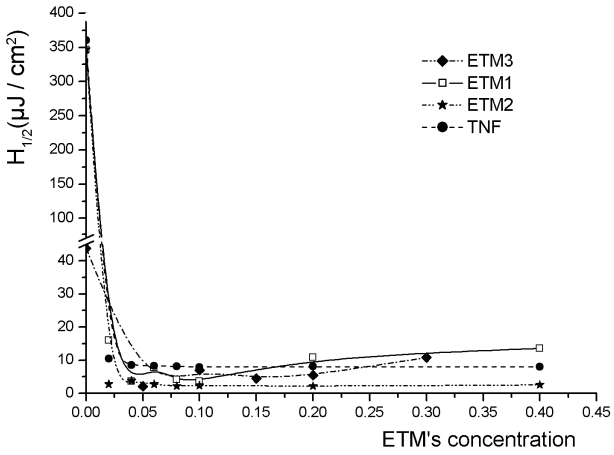

Figure 3. *Half decay exposure as a function of different ETM's Concentration*

For these ETMs, the xerographic performance of ETM2 (2,5,5'-tritert-butyl diphenoquinone) was the best. When exposed at 780 nm and doping concentration at 20 wt.%, the lowest half decay exposures of positive- and negative-charging were 2.2μJ/cm^2 and 2.8μJ/cm^2, respectively. Its xerographic performance was better than that of TNF, ETM1 and ETM2.

As the structure of 2,5,5'-tritert-butyl diphenoquione is very asymmetrical and, due to the large tert-butyl groups, it has better solubility in organic solvents and excellent compatibility with polymers. Therefore, it showed higher sensitivity and more excellent xerographic performance than TNF and 2,5-two methyl,2',5'-diisopropyl diphenoquinone under lower concentrations. There are two electron-transport groups in a of calix[4]arene-based diphenoquinone and shorter transport distance

exists between the two groups, the electrons may drift within the ETM molecular. However, the transport distance between two molecules is longer than small molecule under the same concentration. The electron-transfer capability is decreased and the sensitivity is not high.

Table 1: Effects of CGM Concentration on Xerographic Performances

CGM concentration (wt%)		$H_{1/2}$ ($\mu J/cm^2$)	Vs (V)	Vd (V/s)	Vr (V)
0.5%	+	7.6	607	0.5	7
	-	8.8	1080	56.0	37
1%	+	5	757	13.7	7
	-	8.4	1080	48.5	37
1.2%	+	4.6	1080	14.4	15
	-	11	1080	30.6	45
2%	+	4.6	1080	21.3	7
	-	13.4	1080	41.8	52
5%	+	4.2	1072	28.5	15
	-	39.6	1080	58.0	112
10%	+	4	937	51.3	15
	-	84	1072	79.5	165
15%	+	2.3	787	68.2	22
	-	47.6	772	113.3	120

Table 1 shows the influence of CGM concentration on xerographic performances. H_2Pc was used as CGM, DEH was used as HTM and TNF was used as ETM in the photoreceptor. As indicated by Table 1, half decay exposure dropped evidently, but the dark decay and remainder voltage increased with increasing the concentrations of CGM for positive-charging. However, half decay exposure increased with increasing CGM's concentration for negative-charging. And xerographic performances of photoreceptor for positive-charging were better than those of negative-charging. This suggested that HEM had higher transmission efficiency than ETM. At low CGM concentrations (below 1.2 wt.%), photoreceptor is almost transparent. Charge generation takes place throughout the whole layer, and electron and hole drifted in the same location. At higher CGM concentrations (over 5 wt.%), photoreceptor is opaque as indicated by the corresponding high absorbance and charge generation is limited to the surface. In this case, most photoreceptor layer functions as charge transport layer and only one kind of charge carrier is involved in transport. For positive charging, the main carrier should be the hole and in negative charging, the main carrier would be electron. Based on those results, it is enough to say that at high CGM concentration, photoreceptor is good in transporting hole, but poor in transporting electron. At low CGM concentration, however, photoreceptor is good in transporting both hole and electron.

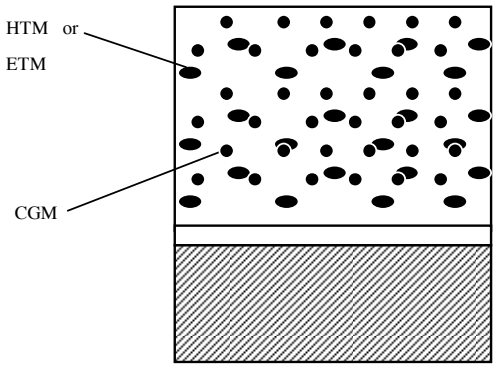

Figure4. *The Structure of bircomponent single-layered organic photorbeceptor*

Xerographic Performance of bicomponent single-layered organic photoreceptor

Figure 4 shows the construction of bicomponent single-layered organic photoreceptor. The main part of the photoreceptor was a polymer matrix doped with charge generation material (CGM), electron transport material (ETM) or hole-transport material (HTM). At higher CGM concentrations (over 15 wt.%), photoreceptor is opaque as showed by the corresponding high absorbance and charge generation is limited to the surface area (approximately 1 μm). In this case, the photoreceptor layer functions as charge transport layer and only one kind of charge carrier is involved in the transportation.

Table 2: Influence of HTM concentration to xerographic performances

HTM concentration (wt%)	$H_{1/2}$ ($\mu J/cm^2$)	Vs (V)	Vd (V/s)	Vr (V)
0%	1.99	1072	2.3	7
25%	0.79	900	31.5	15
30%	0.79	900	29.5	7
35%	0.69	810	29.9	7
40%	0.69	1042	32.2	7
45%	0.59	975	35.1	7

Table 2 shows the influence of the HTM concentration on xerographic performances. The operation of the organic photoreceptor is a positive-charging process. The half decay exposures dropped sharply with the increasing HTM's concentration and became stable when HTM's concentration was over 35 wt.%. The lowest half decay exposure was 0.59μJ/cm^2 at 780 nm wavelength when HTM's concentration was 45 wt.%. ECH was used as HTM in the photoreceptor.

Table 3 shows the relationship of ETM's type and its concentration to xerographic performances. The photoreceptor is negative-charging. In the experiment, the half decay exposures dropped evidently with increasing ETM's concentration. The lowest half decay exposure was 9.5μJ/cm^2 at 780nm wavelength when ETM2's concentration was 40 wt.%. Unfortunately, the remainder voltage of ETMs was too high.

For the construction of bicomponent single-layered organic photoreceptor, the xerographic performances were excellent when it was doped HTM compare with ETM. Half decay exposure was higher in one order and remainder voltage was lower in two orders. The results indicated that the hole-transport ability of HTMs was higher than that of ETMs.

Table 3 Influence of ETMs concentration on xerographic performances

ETMs and concentration (wt%)		$H_{1/2}$ ($\mu J/cm^2$)	Vs (V)	Vd (V/s)	Vr (V)
	0%	51.08	1080	3.9	210
TNF	10%	48.11	952	47.7	210
	20%	22.37	847	53.4	165
	30%	15.44	847	67.1	165
	40%	11.68	817	65.2	157
ETM2	10%	49.30	1080	10.1	195
	20%	29.7	1080	16.1	180
	30%	15.84	1080	27.3	172
	40%	9.60	1080	35.3	172
ETM3	10%	56.83	1080	1.7	277
	20%	24.75	1080	2.6	195
	30%	23.17	1080	4.3	187
	40%	29.30	1080	3.8	210

Conclusion

Fully studies were made on the xerographic performances of tercomponent and bicomponent doped single-layered photoreceptor in which Y-TiOPc was used as CGM, diphenoquinone derivatives were used as ETM. Results showed that photosensitivity was strongly dependent on ETM concentration for the HTM, ETM and CGM doped single-layered photoreceptor. Half decay exposure dropped down sharply with increasing ETM concentration and reached the minimum value when ETM"s concentration was 10 wt%, whereas slightly increased at even higher ETM concentrations. When exposed at 780 nm, the lowest half decay exposures of positive- and negative-charging were fixed at $2.2\mu J/cm^2$ and $2.8\mu J/cm^2$, respectively. For the HTM or ETM and CGM doped single-layered photoreceptor, half decay exposure was found to decrease with the CTM's concentration. The lowest half decay exposure (780 nm) under optimized conditions was 9.6 $\mu J/cm^2$ and $0.59\mu J/cm^2$.

References

[1] Tanaka Masashi, Sakuma Tadashi. Electrophotographic organic photosensitive material with diphenoquinone. US Patent, 5324610. 1994-02-06

[2] H.Kokado, Organic Electron Transfer Process, Chem.Rev.Ser.Vol.2, (Chem.Soc.Jpn.ed.).p.191.194. Gakkaishuppan Center,Tokyo (1988)

[3] Murkami Mutsuaki, Omote Atsushi. Photosensitive material for eletrophotography. EP, 449565. 1991-02-10

[4] Yamaguchi Y, Tanaka H, Yokoyama M. Application of unsymmetrical diphenoquinone derivatives to xerography molecular design of a novel class of polymer dispersible electron transport active compound. J. Chem. Soc. Chem. Canmun. , 222, 1990

[5] Wu Songmei, Wang Wenguang. Study on synthesis of 3,3,5-tributyl-4,4-dibenzoquinone through debutylation. Chemica Reagents. 2003, 25 (2), 109-110.

[6] Wu Ti, Wang Wenguang, Zhang Weimin, Pu Jialing. A Novel Electron Transport Material Based on Calix [4]arene and Its Properties as OPC . Chinese Journal of Scientific Instrument 2004, 25 (4) Extended Edition, 105-108.

Author Biography

Weimin Zhang, male, professor, graduated in East China University of Science & Technology in 1986. He is working in Lab. Printing & Packaging Material and Technology (Beijing area major laboratory), in Beijing Institute of Graphic Communication. His work is focused on organic information recording materials, especially organic photoreceptor, functional materials.