A Novel Ring-Structured Diphenoquione Based on Calix[4]arene as Electron Transport Material Doped in OPC and Its Performances

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Abstract

Two ring-structured diphenoquione derived from the calix[4]arene derivative, i.e. 26,28-dipropoxylate-5,17-bi(m,m'-dimethyl)calix[4] diphenoquione (2a) and 26,28-dipropoxylate-5,17-bi(m,m'-diisopropyl)calix[4] diphenoquione (2b) were synthesized. For compounds 2a and 2b, diphenoquinone was used as electron transport moiety and chemically introduced onto calix[4]arene, which provided a rigid and low freedom aligning base for the electron transport moiety. Experiments results revealed that compound 2b which has isopropyl group exhibited better properties compared with 2a which has methyl groups. Compound 2b was of good solubility in common organic solvents and excellent compatibility with polymers such as PC (a polycarbonate) and Vylon200 (a polyester), and could be doped into the polymers at high concentrations, e.g. over 40 wt.%. Single-layered organic photoconductor (OPC) devices were made with compound 2b, 4-(diethylamino)-benzadehyde-1,1-diphenyl-hydrazone (DEH), Y-type titanium oxide phthalocanine and PC (or Vylon200), which acted as the electron transport material (ETM), the hole transport material (HTM), the charge generation material (CGM) and the bind polymer, respectively. A home-made device, EMS'93, was used to investigate the photoconductivties of the device. Generally, PC was better than Vylon200 as the bind polymer for the OPC devices because the former could make the device have lower and balanced half decay exposures between positive and negative polarities. Investigations also indicated that the half decay exposure of the single-layered OPC devices was strongly dependent on the concentration of the doped ETM, especially at a relatively low concentration, e.g. below 10 wt%. ETM 2b had comparable photoconductities to 3,5-dimethyl-3',5'-isopropyldiphenoquione (MPDQ), a single diphenoquione-structured compound, and 2, 4, 7-trinitro-9-fluorenone (TNF), a traditionally used ETM. The optimal doping concentration of the ring-structured ETM 2b was in the range 15-25 wt.% in PC, while that for MPDQ and TNF, the optimal doping concentration was higher, ranging from 25 wt.% to 30 wt.%. These indicated that the ring-structured ETM 2b have good xerographic properties at low concentrations.

Keywords: diphenoquione, ETM, calix[4]arene, xerographic properties

Introduction

Organic charge transfer material has some applications in many fields, such as organic light-emitting diodes, organic field-effect transistors, solar energy batteries [1~5], organic photoconductors (OPCs) [6~7] and so on. Most commercial available OPCs are negative charging multi-layered devices, which have charge generation layer (CGL) and charge transport layer (CTL). As a result, the preparation process was complex and the image quality was not stable. This may be problematic, especially in high-end applications and O_3 are also produced in charging progress, leading air pollution and other problems. A possible solution is to enable positive charging. This in return requires high quality electron transport materials (ETMs). 2,4,7-trinitro-9-fluorenone (TNF) and its derivatives, traditionally used ETMs, has some disadvantages such as toxicity and relatively poor compatible with polymers [8]. However, Diphenoquinones with an unsymmetrical structure and aliphatic substituents were good ETMs with relatively good charge transport properties and excellent compatibilities with polymers [9~11].

It is well known that calix[n]arene is a macromolecule. A calix[n]arene consisted of repeated phenol units and each of them was linked by methylene bonding in a ring-like architecture [12]. This unique structure provided a rigid platform and its phenol groups can be selectively modified or anchored with other functional groups [13~15], such as electron transport moieties. Therefore, electron transport groups on the rigid platform will be closely packed in a ring-like fashion, and the packing sequence and density can be controlled to meet a specific propose. In this work, two new ring-structured diphenoquiones-containing ETMs were synthesized by using calix[4]arene as the molecular platform and diphenoquiones as the electron transport center. Their electron transport performance were studied and compared with that of other traditional ETMs.

Experimental

5,17-di[(4-hydroxy-3,5-dimethyl)phenyl]-26,28-dipropoxy calix[4]arene (1a), 5,17-di[(4-hydroxy-3,5-diisopropyl) phenyl]-26,28-dipropoxycalix[4]arene (1b) and 3,5-dimethyl-3',5'-isopropyldiphenoquione (MPDQ) were synthesized in our lab. Polymers PC (a polycarbonate C-1400) and Vylon200 (a polyester) were available from Mitsubishi Chemical. 4-(diethylamino)-benzadehyde-1,1-diphenyl-hydrazone (DEH) was brought from ACROS ORGANICS. Y-TiOPc, a Y-type Titanium Oxide phthalocyanine, was prepared according to the literature [16]. And other reagents were commercially available. Structures of compounds synthesized were verified using IR (SHIMADZU FTIR-8400), ^{1}H NMR, ^{13}C NMR (ARIA EMAN FX-300) and MS (Hemeus AEI-MS50). Compounds synthesized in this work are shown in Figure 1 and are described as follows.

26,28-dipropoxylate-5,17-bi(m,m'-dimethyl)calix[4] diphenoquione (2a) and 26,28-dipropoxylate-5,17-bi(m,m'-diisopropyl) calix[4] diphenoquione (2b) were synthesized from 1a and 1b, respectively. To a solution of compound 1a in $CHCl_3$, fresh Ag_2CO_3 adsorbed on silica was added as oxidizer. The mixture was stirred at room temperature and the reaction was closely monitored by thin layer chromatography (TLC). Then the mixture was filtered under reduced pressure. The filtrate was dried by using anhydrous Na_2SO_4 and then, concentrated by evaporating most of the solvent. The remained solution was poured into a large amount of methanol and the precipitate was recrystallized in a mixed solvent of $CHCl_3$ and CH_3OH to give red needle crystals, i.e. the target product, ring-structured diphenoquiones 2a (Yield: 95%). m.p. >300 °C. ^1H NMR ($CDCl_3$) δ : 1.25 (t, 6H, J=7.3Hz, $C\underline{H}_3CH_2CH_2$), 1.60 (s, 12H, $C\underline{H}_3$) , 1.96-2.03 (m, 4H , $CH_3C\underline{H}_2CH_2$), 3.56-3.62 (d , 8H , $ArC\underline{H}_2Ar$), 3.78 (t, 4H, J=6.6Hz, $CH_3CH_2C\underline{H}_2$), 6.62 (m, 2H, J=7.5Hz, $Ar\underline{H}$), 6.90 (s, 4H, $Ar\underline{H}$), 7.65 (s, 4H, $Ar\underline{H}$), 7.70 (s, 4H, $Ar\underline{H}$). ^{13}C NMR ($CDCl_3$) δ : 186.8, 156.8, 141.3, 140.9, 138.3, 136.2, 135.6, 130.9, 130.3, 129.1, 128.2, 123.0, 75.6, 29.7, 24.2, 17.2, 11.2. IR (KBr) υ : 2918.1, 1635.5, 1606.6 (C=O), 1576.7, 459.1 cm^{-1}. P-SIMS-NBA: m/z: 746.3601660[M^++H].

2b was synthesized from 1b by the same method. (Yield: 96.5%) m.p. >300 °C. ^1H NMR (CDCl3) δ : 1.10 (t, 6H, J=7.4Hz, $C\underline{H}_3CH_2CH_2$), 1.21 (d, 24H, J=6.2Hz, $CH(C\underline{H}_3)_2$), 1.81-2.04 (m, 4H, $C\underline{H}(CH_3)_2$), 3.24-3.29 (m, 4H, $CH_3C\underline{H}_2CH_2$), 3.71 (t, 4H, J=6.9Hz, $CH_3CH_2C\underline{H}_2$), 3.50-3.83 (s, 8H, $ArC\underline{H}_2Ar$), 6.58 (t, 2H, J=7.4Hz, $Ar\underline{H}$), 7.69 (s, 4H, $Ar\underline{H}$), 7.82 (s, 4H, $Ar\underline{H}$). ^{13}C NMR ($CDCl_3$) δ : 185.4, 156.7, 148.2, 142.4, 136.6, 136.2, 131.0, 130.9, 129.4, 128.6, 126.0, 122.8, 76.1, 27.4, 24.2, 22.2, 22.1, 11.1. IR (KBr) υ : 2960.5, 2927.7, 2869.9, 1598.9 (C=O), 1460.0 cm^{-1}. P-SIMS-NBA: m/z: 879.4594804[M^++Na].

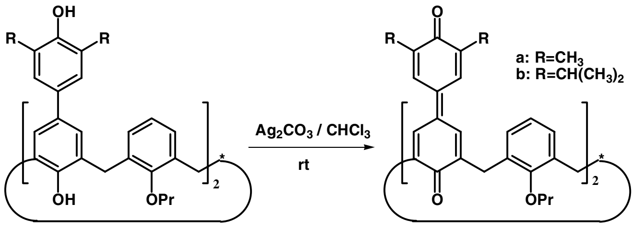

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Figure 1. Synthetic Route of Ring-structured ETMs

Compatibility of synthesized ETMs with polymers was evaluated by measuring the absorbance (500-900 nm) of the polymer films coated on glasses using a Shimadzu UV-2501PC. The polymer films were prepared by dissolving measured amount of the ring-structured ETMs (20, 30, 40, 50 wt.% in polymers) in polymer solutions (11 wt.% in THF for PC and 20 wt.% in THF for Vylon200) and then spin-coated onto a carefully washed slide glass, followed by drying at 80 °C for 4 h.

The OPC devices were prepared with Y-TiOPc, DEH and ETMs, which were charge generate material (CGM), hole transport material (HTM) and ETMs, respectively. Single-layered OPC device was prepared according to following procedures: polymer, ETM and HTM were completely dissolved in THF and then, CGM was added. The suspension was subject to mechanical agitation for 30 mins followed by supersonic dispersion treatment for 10 mins, and coated onto a 0.15 mm thick aluminum substrate by dip coating. The dry film was dried at 80 °C for 4 h in an open air oven and was 15~20 μm (Taylor Hobson FTS-S3c) thick.

The xerographic performances of OPCs device were measured by using a home-made device called EMS'93 (Figure 2), which was equipped with Trek 610C high voltage supplier, Trek 362A surface potential meter with a transparent probe (Trek 3629). A 400W xenon lamp and a suitably integrated filter set (neutral absorbance filter and interference filter) were used to generate monochromatic radiation. Light intensity was measured by DR-1600 (Gamma Scientific). Exposure wavelength and discharging voltage were fixed at 780 nm and ±5300 V, respectively. Static charge continuously accumulated to reach maximum saturated surface voltage (Vs). And then stopped charging, there will be some extent decrease of surface voltage before exposing, which is called dark decay. v_d is the dark decay rate and V_0 is the surface voltage at start of exposing. When exposure is imposed, the surface voltage decreases fast, i.e. photo-decay. After exposing for 15 s, there is residual voltage (Vr) on the surface of the OPC device. $E_{1/2}$ is the half decay exposure, equal to exposure light intensity multiples the D-value of time from V_0 to $1/2V_0$. Vs, v_d, Vr and $E_{1/2}$ are all the indexes of xerographic performances of OPC devices.

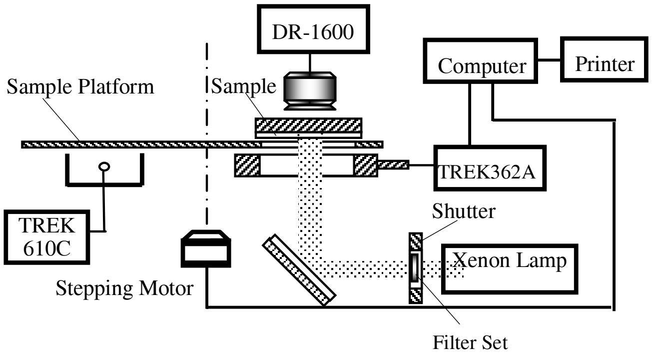

Figure 2. A Schematic Description of EMS'93

Results and Discussion

Organic solvents are commonly used as the solvent for preparing OPC devices. 2a and 2b showed excellent solubility in common organic solvents such as THF, $CHCl_3$, 1,2-dichloroethane and 1,4-dioxane, and solutions with a concentration over 10.wt.% could be obtained easily. This would facilitate the preparation of OPC devices.

It is known that crystallization or separation of ETM molecules out from the polymer matrix will result in reduction of xerographic performances of OPC devices. When there are any crystallization of ETM molecules or separation from the polymer matrix, the film will become heterogeneous, and therefore there is equal absorbance at longer wavelengths where neither the ETM nor the polymer absorbed, in the absorbance spectrum. On the other hand, when there is no crystallization or separation, the value of ABS is zero at longer wavelengths (500-900 nm), where ETMs and polymers have no absorbance. According to the relationship between equalized absorption at longer wavelengths and doping concentration of ETMs in the polymer matrix, compatibilities of ETMs with polymers can be identified effectively.

The Uv-vis absorbance spectra revealed that the maximal solubility of 2a in Vylon200 was less than 20 wt.% and that in PC was less than 30 wt.%. For 2b was over 40 wt.% in Vylon200 and over 50 wt.% in PC. This indicated that 2b was highly compatible with the polymers and the compatibilities of 2b with polymers, PC and Vylon200, were better than those of 2a, which was mainly brought by the different substitutes (R) of diphenoquinone units in molecule structures of 2a and 2b, i.e. methyl and isopropyl. Further, the compatibility of 2b with PC was better than that with Vylon200.

ETMs have different compabilities with different polymers, brought the different influences on xerographic performances of OPC devices. Table 1 shows xerographic performances data of single-layered OPC devices with different polymers, i.e. PC and Vylon200, used as polymer binders. The coated films were controlled at the same thickness by 11 wt.% in THF for PC and 20 wt.% in THF for Vylon200, respectively.

In Table 1, the values of Vs, v_d, and Vr had no essential difference. And $E_{1/2}$ was found dependent on the polymer binders. PC was generally better than Vylon200, as indicated by its lower and balanced half decay exposures between negative and positive polarities, i.e. 4.2×10^{-6} J/cm^2 and 3.7×10^{-6} J/cm^2. This result reasonably came from the fact that the ring-structured diphenoquiones were more compatible with PC than with Vylon200.

Table 1: Xerographic Performances Data of OPC Devices with Different Polymer Binders

Polymer	Charge Type	Vs (V)	v_d (V/s)	$E_{1/2}$ (10^{-6}J/cm^2)	Vr (V)
PC	Negative	690	28.7	4.2	60
	Positive	540	21.8	3.7	30
Vylon200	Negative	522	31.9	10.8	52
	Positive	660	13.2	5.2	60

Note: Y-TiOPc/DEH/THF = 0.6/25/909 (in wt.), 2b/DEH = 1/2 (in mol). Exposure light intensity: 6.30×10^{-6} w/cm^2.

Table 2: Xerographic Performances Data of OPC Devices with Different Concentration of CGM

Y-TiOPc (wt% in PC)	Charge Type	Vs (V)	v_d (V/s)	$E_{1/2}$ (10^{-6}J/cm^2)	Vr (V)
0.2	Negative	435	36.8	9.2	37
	Positive	375	22.6	8.6	50
0.6	Negative	735	27.3	4.3	67
	Positive	570	15.9	3.4	52
1.2	Negative	597	26.6	3.0	50
	Positive	577	10.5	2.3	30
1.8	Negative	675	31.8	3.2	50
	Positive	550	11.2	2.2	30
2.4	Negative	630	35.2	3.3	52
	Positive	517	13.4	2.3	30

Note: DEH/PC = 25/100(in wt), 2b/DEH = 1/2 (in mol). Exposure light intensity: 6.60×10^{-6} w/cm^2.

Though the doping concentration of CGM is very low, it still has influence on xerographic performances. With the increase of the doping concentration of CGM from 0.2 to 2.4 wt.% in PC (Table 2), the xerographic performances were improved apparently and then changed little, in which $E_{1/2}$ decreased greatest to about one fourth and others changed little or below one half, and the concentration of CGM had an optimal value, i.e. 1.2 wt.%/PC. $E_{1/2}$, Vr and *vd* reached minimal values, i.e. 3.0×10^{-6} J/cm^2, 50 V and 26.5 V/s by negative charging and 2.3×10^{-6} J/cm^2, 30 V and 10.5 V/s by positive charging, respectively, when Y-TiOPc's concentration was about 1.2 wt.% relative to PC. The values of $E_{1/2}$ by positive charging were lower than those by negative charging from 0.2 to 2.4 wt.%/PC, which indicated that OPC devices doped with 2b tended to be the positive charging type.

Figure 3 shows the influence of molar concentration of different transport centers in PC on $E_{1/2}$. With increasing doping concentration of transport centers (DCTC), $E_{1/2}$ decreased first and then increased after having reached a minimum, regardless of the polarity of surface charge and different ETMs. When $E_{1/2}$ reached the minimum values, The DCTC was somewhere in 0.07~0.1 mol%/g (about 25~30 wt.% in PC) for MPDQ and TNF and

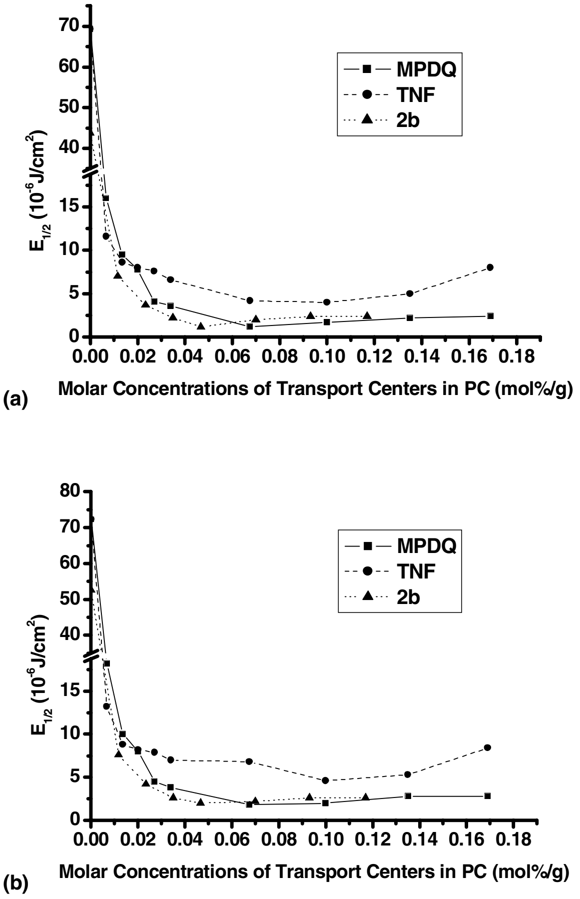

Figure 3. the Influence of Molar Concentration of Different Transport Centers in PC on $E_{1/2}$. (a) by positive charging (b) by negative charging. PC/THF = 11/100(in wt.), Y-TiOPc:DEH:PC = 1.2:25:100(in wt), Exposure light intensity I = 10.00×10^{-6} w/cm^2

in 0.04~0.06 mol%/g (about 15~25 wt.% in PC) for 2b, respectively. And the minimal values of $E_{1/2}$ for 2b and MPDQ were smaller than that for TNF. At relatively higher DCTC (> 0.1 mol%/g, about 40 wt.% in PC) xerographic performances of OPC devices doped with 2b were poorer than those with MPDQ for the values of $E_{1/2}$ for MPDQ were lower than those for 2b. And the values of xerographic performances by positive charging were also lower than those by negative charging, which indicated that OPC devices doped with 2b preferred to be the positive charging type.

2b has two transport centers, while MPDQ (or TNF) has only one center, hence the actually molar doping concentration of 2b compound was half of that of MPDQ or TNF at the same DCTC. This result in photo-produced electrons had to hop longer distance in the device doped with 2b than doped with TNF or MPDQ. The experiment results indicated that 2b trends to be more pronounced at relatively lower doping concentrations and 2b was more sensitive than TNF and MPDQ. And MPDQ has the same molecular structure with the transport center of ring structure ETM 2b. It was hard to understand why 2b was more sensitive at lower doping concentrations than at higher concentrations. At lower doping concentrations, adjacent hoping centers (2b) were separated at longer distance, unfavorable for photogenerated electron to hop and therefore promoting sensitivity. This unusual behavior of 2b might come from the good compatibility between calix[4]arene-based diphenoquinone and other components of the device or from the unique structure of the calix[4]arene-based ring-structured diphenoquinone, in which the distance of two electron transport centers were about 3~4 Å and equivalent to fix two DMDQ molecules on a low freedom aligning flat form.

Conclusion

Two ring-structured diphenoquione based on calix[4]aren were successfully synthesized and their compatibilities and xerographic properties were systematically studied. 2b was of good solubility in common organic solvents and excellent compatibility with polymers, such as PC and Vylon200, and was able to be doped at high concentrations, e.g., more than 40 wt.%. When applied in single-layered photoreceptor, the ring-structured ETM 2b, with two diphenoquione units, isopropyl group and *p*-propyl ether group was of equal or better performances than MPDQ and TNF. The optimal concentration of the ring-structured ETM 2b was 15~25 wt.%, while that for MPDQ and TNF was 25~30 wt.%, indicating that the ring-structured ETM 2b was especially good at suitably low concentrations and was likely to be the positive charging type. In 2b's molecular structure diphenoquinone was used as electron transport moiety and chemically introduced onto calix[4]arene, which provided a rigid and low freedom aligning base for the electron transport moiety. The unique structure allowed the electron transport moieties to be closely packed and uniformly aligned. This unique structure was believed to be the main contribution to the promoted compatibility and higher sensitivity at lower doping concentrations.

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