

Organic Pigment Nanoparticle Thin Film Devices via Lewis Acid Pigment Solubilization and *In Situ* Pigment Dispersions

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We introduce a new pigment processing approach, namely Lewis acid pigment solubilization (LAPS), for the fabrication of organic pigment thin film devices. The process involves the solubilization of an organic pigment in a Lewis acid/nitromethane solution. The resulting solution can be used to solvent cast pigment/Lewis acid thin films, which are then washed with an aqueous solution to remove the Lewis acid and give the final pigmented layers. Alternately, the pigment/Lewis acid solution can be used for acid pasting to give pigment wet cakes, which can then be used for preparing *in situ* pigment dispersions suitable for solvent coating. A wide range of organic pigment thin film devices can be fabricated using these processes, as we demonstrate in this article for the fabrication of organic photoreceptors.

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Introduction

Organic dyes and pigments have a wide range of commercial applications in coatings, printing, information storage, and display technology.¹ Pigments have many advantages over dyes, such as light and waterfastness, color strength, photosensitivity, and overall stability. However, pigments are more difficult to process than dyes mainly because pigments are highly insoluble. The available processes for the deposition of pigment thin films have been complicated and limited. Three most commonly used processes are high-energy pigment attrition, sulfuric acid pasting, and pigment flushing and the pigment sublimation. The pigment dispersions obtained from the first two processes are then used to cast pigmented layers by conventional coating processes. Electrochemical deposition of pigment thin films using aqueous pigment dispersions have also been reported.² Although fine pigment particles can be obtained by prolonged attrition, the resulting pigment dispersions often reaggregate in time. Pigment sublimation can give pigment layers with high purity and uniformity; however, it is a complicated and expensive manufacturing proposition particularly for large-scale production operations. In addition to the above physical processes, chemical processes such as side chain routes and precursor routes have also been used to overcome the processability problems of pigments. The former involves the direct attachment of flexible or bulky substituents onto pigment molecules via stepwise organic synthesis.³ The latter involves the preparation of a soluble precursor, which can be converted to the insoluble parent pig-

ment by heat or radiation, such as the latent pigment work reported recently for pyrrolo[3,4-C]pyrroles.⁴ We have used these two chemical processes to overcome the processability issue associated with conjugated polymers such as poly(p-phenylene vinylenes).⁵ However, the chemical processes are often system specific and are thus less generally useful than the physical processes.

We reported a new simple physical process, namely Lewis acid pigment solubilization (LAPS), for the deposition of pigmented thin films composed of pigment nanoparticles in a recent communication.⁶ Here we report the extension of LAPS for the preparation of pigment dispersions suitable for coating a charge generation layer of an organic photoreceptor by acid pasting of pigment/Lewis acid solutions. LAPS is an adaptation of Lewis acid polymer solubilization for depositing rigid rod heterocyclic polymer thin films.⁷ We have found that LAPS is generally applicable to many heterocyclic pigment classes such as phthalocyanines, perylene-*bis*-midazoles, azos, and the like.⁸ We are amazed by the fact that many pigment classes can be handled like dyes through LAPS, blurring the common definitions of dyes and pigments. In this article, we demonstrate the use of LAPS and *in situ* pigment dispersions to fabricate multilayered organic photoconductors (OPC) with good sensitivity, high cyclic stability, low dark decay, and residual charges. We envision that LAPS has a tremendous potential for the fabrication of other pigment-based organic semiconductor devices such as light-emitting diodes,^{9–10} photodiodes, solar cells,¹¹ field effect transistors,¹² and the like.

Experimental

Pigment/aluminum chloride (AlCl₃) complex solutions were prepared by magnetic stirring a mixture of a pigment, AlCl₃, and nitromethane and optional methylene chloride in capped vials (20 ml) in a glove box under nitrogen atmosphere for 12–16 h. at room temperature.

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TABLE I. Composition for Pigment/Aluminum Chloride Solution

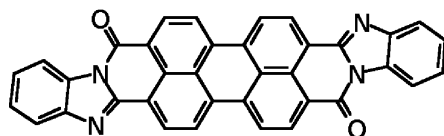
	Solution 1 ^a	Solution 2 ^b	Solution 3 ^c	Solution 4 ^d	Solution 5 ^e	Solution 6 ^f	Solution 7 ^g
Pigments (g)	0.26	0.39	0.52	0.29	0.29	0.17	0.30
AlCl ₃ (g)	0.39	0.59	0.78	0.39	0.39	0.39	0.39
Nitromethane (ml)	8	8	8	10	10 10	10	—
Methylene chloride (ml)	2	2	2	—	—	—	—

a: bisbenzimidazole perylene (BZP); b: titanyl phthalocyanine; c: vanadyl phthalocyanine;

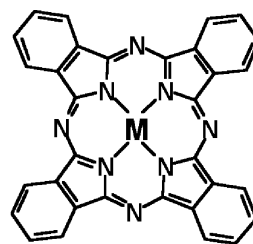
d: copper phthalocyanine; e: hydroxy gallium phthalocyanine; f: 2,9-dimethylquinacridone; g: Pigment Yellow 97

TABLE II. Compositions of BZP/AlCl₃ Solutions

Pigment & Reagents	Solution 8	Solution 9	Solution 10	Solution 11	Solution 12
BZP (gram)	0.26	0.39	0.52	6.5	3.0
AlCl ₃ (gram)	0.39	0.59	0.78	10.0	4.5
nitromethane (ml)	6	6	6	250	90
MeCl ₂ (ml)	4	4	4	0	0
BZP (wt%)	2.0	3.0	3.9	2.2	2.75

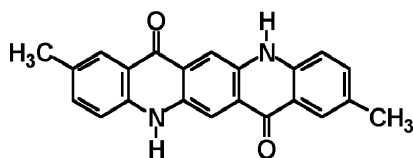


(a)

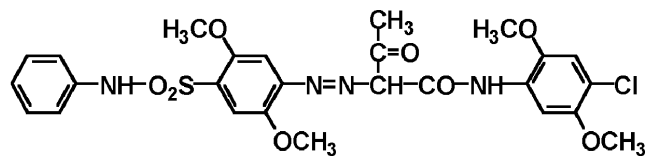


(b) M = TiO; (c) M = VO

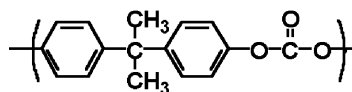
(d) M = Cu; (e) M = GaOH



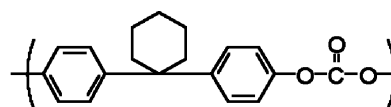
(f)



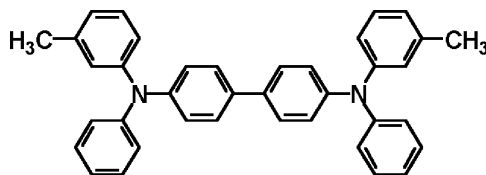
(g)



(h)



(i)



(j)

Figure 1. Chemical structures of (a) BZP (*cis*-form not shown); (b) titanyl phthalocyanine; (c) vanadyl phthalocyanine; (d) copper phthalocyanine; (e) hydroxy gallium phthalocyanine; (f) 2,9-dimethylquinacridone; (g) Pigment Yellow 97; (h) polycarbonate; (i) PCZ; (j) TPD.

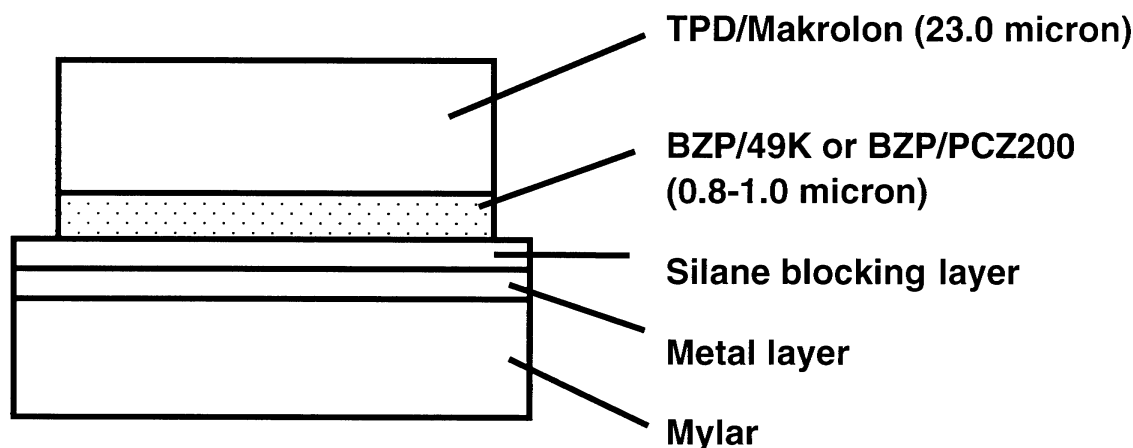


Figure 2. A typical OPC device structure.

A set of pigment solutions using *bis*(benzimidazole)perylene (BZP), titanyl phthalocyanine, vanadyl phthalocyanine, copper phthalocyanine, hydroxy gallium phthalocyanine, 2,9-dimethylquinacridone, and Pigment Yellow 97¹³ were prepared as summarized in Table I. The molar ratio of the pigment to AlCl_3 was 1:6 in all cases. These solutions had about 2 wt% of pigment and easily passed through 0.45 μm filters. The chemical structures of the pigments are shown in Fig. 1.

Our studies focus on BZP because it is one of the most photosensitive and stable pigments known.^{14,15} Table II summarizes the compositions for three representative BZP solution mixtures. Solution 8, having about 2 wt% BZP, was easily filtered through a 0.45 μm filter, but solutions 9 and 10 with higher pigment concentrations could not be easily filtered. This indicated that BZP can be almost completely solubilized at about 2 wt% and that BZP/ AlCl_3 complex may form aggregates at higher pigment concentrations. Being in complete solution, solution 8 should enable one to deposit thin films with the highest degree of uniformity and controlled thickness by means of spray or dip coating. However, we were limited to draw bar coating and thus chose the unfiltered solution 10 for the fabrication of OPC devices in order to achieve BZP layers (0.8–1.0 μm thick) with suitable optical density.

Solutions 11 and 12 were unfiltered and used for the preparation of *in situ* pigment dispersions as follows. Solution 11 was poured into water (1000 ml) while homogenizing with a Brinkmann homogenizer at 8,000 rpm. Homogenization was continued for 1 min. The resulting pigment mixture was evenly divided into three 500 ml centrifuge bottles and centrifuged at 5,000 RPM for 15 min. The combined pigment wet cakes were washed with 1.2% aqueous ammonium hydroxide solution (1000 ml) by homogenizing at 8,000 RPM for 1 min. The centrifuge process was repeated followed by a second wash with methanol (1000 ml). The pigment was collected by centrifuge as wet cakes. Into a 4 oz. amber bottle were added the pigment wet cakes (12.0 g), THF (48 ml.) and PCZ-200 (0.3 g), and 1/8 in. stainless steel shot (300 g). The mixture was ball milled for 1 h to give an *in situ* pigment dispersion A. PCZ-200 is a bisphenol Z polycarbonate (Fig. 1) from Mitsubishi Chemical with an average molecular weight of about 200,000. Solution 12 was processed similarly by pouring into water (500 ml). The pigment was washed first with water (500 ml each) and then by methanol (500 ml). The collected wet cakes

were mixed in with THF (19-ml.) containing PCZ-200 (0.15 g) by ball milling for 1 h to give BZP **dispersion B**.

All the devices were deposited on 49K/SBL/Ti/MYLAR[®] substrate with the following specification: MYLAR[®] films (75 μm) with Ti coatings of 200–300 Å were overcoated with a 2-aminopropyltriethoxysilane blocking layer (200–500 Å) and then an adhesive undercoat layer (200–500 Å) of polyester 49K (DuPont) to give 49K/SBL/Ti/MYLAR[®] substrates. A Gardner mechanically driven film applicator enclosed in a plexiglass acrylic box with an attached cover was used for depositing BZP/ AlCl_3 layers onto Mylar[®] substrates using solution 9. A 49K/SBL/Ti/MYLAR[®] substrate (appx. 8 × 11.5 in.) was placed on the vacuum plate of the Gardner coater and a size 0.003 Bird film applicator was placed on top of the substrate. Approximately 1 ml of solution 9 was applied with a pipet along the Bird film applicator onto the substrate. The as cast BZP/ AlCl_3 layers were washed in a water tray for 5 min followed by a second wash for 5 min, either with 2% Na_2CO_3 , with 2% NH_4OH or with deionized water at 50°C then air dried to give BZP charge generation layers (CGL). The charge transport layers (CTL) were then deposited by draw bar coating using a 0.004 size Bird film applicator in the enclosed coating box with a solution of TPD (5.0 g), Makrolon (5.0 g) and methylene chloride (57 g). The resulting device was dried in a forced air oven at 100°C for 30 min to give OPC devices with a structure depicted in Fig. 2. Similarly, dispersion A or B was used to coat BZP layers followed by the coating of TPD layer. The thickness of the BZP layers was about 2.0–3.0 μm and the TPD layer was about 27–30 μm in all cases. The chemical structures of polycarbonate, PCZ 200, and TPD are shown in Fig. 1.

Xerographic measurements were made on a (rotating) cycling scanner at 20 RPM, at 20°C, and 35% RH, using 3 × 4 in. samples of the imaging member prepared as described herein. The samples were corona charged with a negative, constant current to an average charge of 105 nC/cm², which is equivalent to an electric field of 40 V/ μm . The surface potential of the samples was monitored with Monroe Electronics non-contacting voltmeters (Model 144) placed at various positions around the circumference of the drum, corresponding to various times from charging. An exposure to monochromatic light was located 45 degrees from charging or 0.375 sec after charging and a white light erasure at 2.53 sec after charging. Voltage probes were located to monitor the

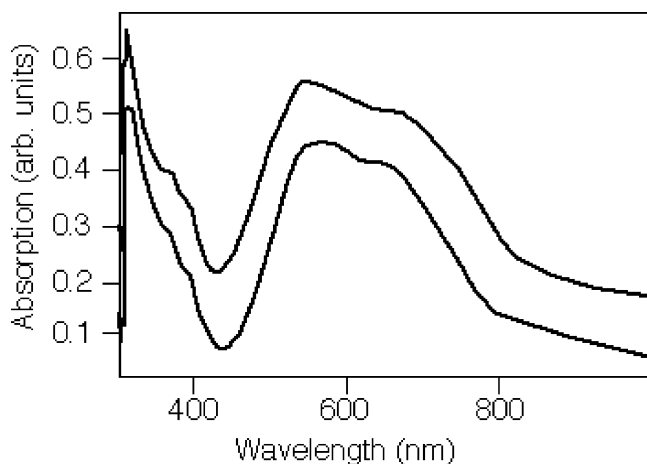


Figure 3. The UV-Vis spectra for BZP (top) and BZP/AlCl₃ complex (bottom).

voltages after exposure and erase. The test sequence and data collection were controlled by computer. Monochromatic light exposure consisted of a collimated Xenon lamp, first order interference filters with a 10 nm halfwidth, neutral density filters to control the intensity of the light, a shutter, and a beam splitter with a calibrated PIN Si diode monitoring the exposure.

Results and Discussion

As can be seen from Table I, a wide range of heterocyclic pigments and an azo pigment have been dissolved by LAPS at about 2 wt% of pigment loading. Solutions with this relatively high pigment percentage can be used for a wide range of coating applications. The solubilization of heteroatom-rich pigments in AlCl₃/nitromethane solution can be attributed to a site-specific Lewis acid-base reaction to form a localized coordinated covalent bond between the AlCl₃ and a heteroatom. This is in agreement with the report for the Lewis acid polymer solubilization of rigid rod heterocyclic polymers.⁷ The UV-VIS spectra of BZP and BZP/AlCl₃ (Fig. 3) are essentially identical without forming new transition bands. The IR spectra BZP and BZP/AlCl₃ are significantly different (Fig. 4). The strong carbonyl peak of BZP at about 1700 cm⁻¹ may have shifted to 1550 cm⁻¹ and became relatively weak in the BZP/AlCl₃ complex. We focus our study on BZP because it is one of the most photosensitive and stable pigments known.^{13,14}

We investigated the Al and Cl atom concentrations for the as cast BZP/AlCl₃ films as well as aqueous washed films. The as cast films showed about 2.0 atomic percent of Al and Cl. The washed films showed non-detectable Al and Cl, indicating that their concentrations are less than the detecting limit of XPS of 0.1 atomic%. However, we were able to detect the presence of traces of Al and Cl (2000–5000 ppm) by energy dispersive X-ray analysis (EDXA) using an X-ray beam of 10kV. Both XPS and EDXA results indicate that short time (5 min) aqueous washing is highly effective in decomposing and removing AlCl₃.

The scanning electron micrographs of the pigment layers showed highly coherent film-like images with no detectable individual pigment particles, indicating a very high degree of uniformity for the pigment layers. The BZP layers deposited via LAPS or *in situ* dispersions showed significantly broader x-ray diffraction

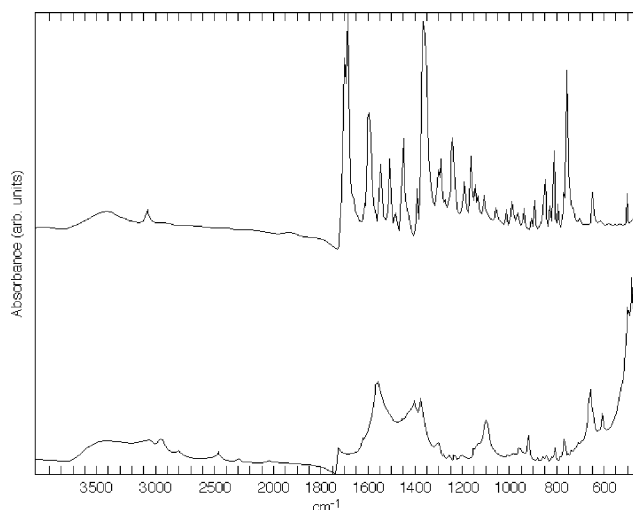


Figure 4. The IR spectra of BZP (top) and BZP/AlCl₃ complex (bottom).

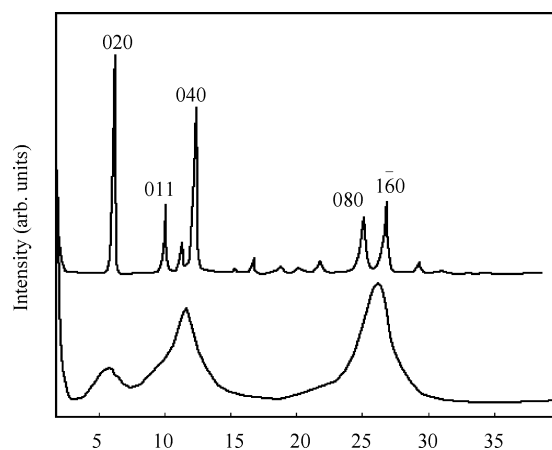


Figure 5. The X-ray diffraction patterns for attrited BZP (top) and LAPS deposited BZP (bottom).

peaks than those of the sublimed BZP, as shown in Fig. 5. From the X-ray diffraction patterns, we estimated an average crystallite size for BZP from LAPS of about 50 nm, which is at least five times smaller than that for the attrited or sublimed BZP.⁶

We found that the pigments listed in Table I can also be dissolved in trifluoroacetic acid (TFA) and investigated the possibility of depositing a pigment layer from a pigment/TFA solution. However, we were not able to obtain coherent pigment thin films from the pigment/TFA solution. The TFA deposited coatings showed islands of pigment agglomerates. This may be due to rapid evaporation rate of TFA and poor wetting of the adhesive layer by TFA.

In principle, the pigment/TFA solutions can be used to prepare *in situ* pigment dispersions according to the procedure described in the experiment for the preparation of *in situ* BZP dispersions. Sulfuric acid pasting from sulfuric acid to prepare pigment-wet cakes is a well-known industrial process. Lewis acid pasting pigment/AlCl₃/nitromethane solution is a new way to prepare pigment wet cakes. We do not know if this new process has an overall advantage over sulfuric acid pasting, but we noticed that AlCl₃/nitromethane solution can

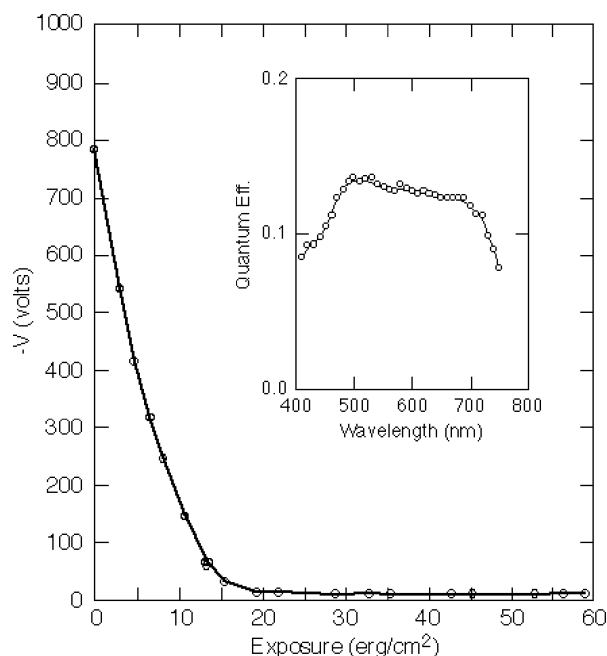


Figure 6. The photodischarge curve using 670 nm light, measured 0.375 sec after exposure for device IV and the corresponding quantum efficiency plot (inset).

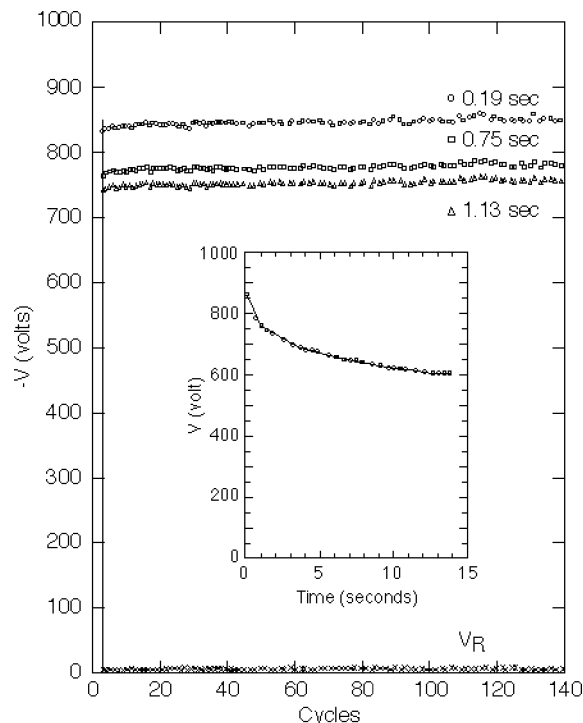


Figure 7. Cycling voltage data for device IV and the corresponding dark discharge (inset).

TABLE III. Xerographic Data*

Device No.	V_R	$V_{0.2}$	Dark Decay (1 sec)	Sensitivity at 670 nm			Sensitivity at 780 nm		
				S	$E_{0.5}$	$E_{0.12}$	S	$E_{0.5}$	$E_{0.12}$
I	4	845	27	60	9	21	16	29	70
II	5	885	15	32	15	35	9	71	170
III	5	864	23	50	11	24	13	46	110
IV	4	849	90	73	5	12	22	17	40
V	5	848	64	45	19	27	11	53	110

* V_R = Residual voltage (in volts)

$V_{0.2}$ = The initial surface potential measured at 0.2 sec (in volts)

S = The initial slope of the discharge curve (in V/erg/cm²)

$E_{0.5}$ = The light exposure required to discharge from 800 to 400 V (in erg/cm²)

$E_{0.12}$ = The light exposure required to discharge from 800 to 100 V (in erg/cm²)

be poured quickly and safely into cold water without significant exothermic reaction. This would not be the case for sulfuric acid. Although it is possible to select a surfactant that may stabilize the pigment particles and enhance the sensitivity of the resulting devices, we did not use surfactants in the aqueous phase during acid pasting because selecting a suitable surfactant could be very time consuming. The *in situ* pigment dispersions were ball milled for 1 h before being used for coating. We have used the *in situ* pigment dispersions for depositing charge generation layers in our dip coating pilot plant. This implies that the pigment dispersions are compatible with traditional OPC manufacturing based on dip coating.

Xerographic measurements were performed on five BZP OPC devices I–V and the data are summarized in Table III. Devices I–III were fabricated via LAPS and devices IV and V were from *in situ* pigment dispersions A and B, respectively. The BZP layers in devices, I, II, and III were, respectively, second washed either with 2% Na₂CO₃, with 2% NH₄OH or with deionized water at

50°C. Because the xerographic data for all the devices were similar, we use the photodischarge curve (Fig. 6) and the voltage versus cycling plots (Fig. 7) for device IV as examples for discussion. Figure 6 is a photodischarge curve observed 0.75 sec after charging and 0.375 sec after exposure to 670 nm light for device IV. The slope of discharge (S), which corresponds to the sensitivity of the device, is 73 V/erg cm² and the light exposures required to discharge from 800 to 400 V ($E_{0.5}$) or to 100 V ($E_{0.12}$) are 5 or 12 erg/cm², respectively, as shown in Table III. The exposure is inversely proportional to the photosensitivity. The sensitivity and exposure data at 780 nm are also given in Table III. Similar xerographic testing was performed for other devices and the resulting data are listed accordingly. The inset of Fig. 6 shows the quantum efficiency plot against wavelength of the discharge light. The efficiency plot is in excellent agreement with the absorption spectrum of BZP (Fig. 3).

Figure 7 is a typical voltage versus cycling plot for device IV, showing four voltages, three measured after

charging, and one after light erasure. As is evident in Fig. 7, the voltages are exceptionally stable with cycling; the random variation of less than 10 V is due to 1% variation in the corotron charging and systematic variation in voltage is less than 1 V. Over 1,000 cumulative cycles the voltage changed by less than 10 V under constant charge conditions. The residual voltage remained at less than 5 V over the entire 1,000 cycle test. Such cyclic stability and low residual voltage were also observed for all other devices (see Table III). The dark discharge was monitored by turning off the erase light and charging and observing the voltage over several cycles. The inset shows a typical dark discharge, with an average dark discharge over 10 sec of 90 V/sec.

The different xerographic data for devices I–III are likely to be related to the different aqueous washing methods. Among the three devices, the Na_2CO_3 washed device I showed the highest sensitivity, while the NH_4OH washed device II showed the lowest sensitivity. Device IV, which was prepared from an *in situ* BZP dispersion, showed the highest sensitivity with $E_{0.5}$ of 5 erg/cm². Although the sensitivity in all cases is still lower than that for the sublimed BZP OPC with $E_{0.5}$ of 3.5 erg/cm² reported by Loutfy and co-workers,¹⁵ one should be able to optimize the sensitivity of the LAPS OPC devices through fine tuning the coating and the washing parameters. For example, the use of solutions with complete pigment solubilization (such as solution 8) may enable the deposition of pigment coatings with the highest degree of uniformity and controlled in thickness. These in turn may give rise to devices with improved photosensitivity.

The dark discharge for devices IV and V are significantly higher than those for devices I–III. This may be due to high concentrations of residual impurities in the BZP layers deposited from the *in situ* dispersions. An OPC device based on a BZP/ AlCl_3 layer without water washing showed too rapid a dark decay rate to be characterized by the xerographic measurements. This indicates that the impurities resulting from the decomposition of AlCl_3 caused rapid dark decay. Note the near IR (780 nm) sensitivity for the LAPS OPC devices. This has been observed for devices with vacuum deposited BZP layers.¹⁶

In summary, we have introduced a new pigment processing approach, LAPS, for the fabrication of organic pigment thin film devices. A LAPS process involved the solubilization of an organic pigment in a Lewis acid/

nitromethane solution. The resulting solution was used to cast pigment/Lewis acid thin films, which were then washed with aqueous solutions to remove the Lewis acid and give the final pigmented layers. A pigment/ AlCl_3 /nitromethane solution can also be used for acid pasting to prepare *in situ* pigment dispersions. It should be possible to fabricate a wide range of organic pigment thin films devices via LAPS, as we have demonstrated in this paper for the fabrication of multilayered OPCs. ▲

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