

Development of Azo Pigments for High Performance Organic Photoconductors (OPC)

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We developed a novel coupler, hydroxyperinone, 2- and/or 5-hydroxy-7H-benz[de]benzimidazo[2,1-a]isoquinoline-7-one and synthesized a bisazo pigment from the novel coupler. The OPC using this bisazo pigments showed better characteristics in sensitivity and cyclic stability than the OPC using bisazo pigments derived from Naphthol AS. ¹³C NMR spectra of these bisazo pigments indicated that the dominant tautomer of the new bisazo pigment in the solid state was different from those of other bisazo pigments. The difference in tautomers reflects their characteristics. We designed and synthesized a unique highly sensitive unsymmetrical bisazo pigment having a large dipole moment in the excited state, on the basis of the photocarrier generation process model. Thermally stimulated current measurements were applied to elucidate factors for high sensitivity.

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Introduction

Electrophotography is a key technology for copying and for non-impact printing on plain paper. Many improvements and developments have been made since Chester F. Carlson invented the electrophotographic process in 1938.¹ Photoconductive insulating materials are used as photoreceptors in this process. Inorganic photoconductors such as selenium alloys, cadmium sulfide, zinc oxide and amorphous silicon have been used. These inorganic photoconductors have been gradually replaced by organic photoconductors (OPCs) since IBM introduced the first OPC for copiers in 1970. Many companies have developed and commercialized OPCs for copiers and laser printers. In recent years, OPCs have become dominant with improvement of their characteristics.^{2,3}

The first organic photoreceptor was a single layered photoconductor based on poly-N-vinylcarbazole and 2,4,7-trinitrofluorenone (PVK/TNF).⁴ The lifetime of this photoreceptor was several thousand copies and the sensitivity was not high enough. The next generation organic photoconductors were developed in 1970s.^{5,6} They are dual layered organic photoconductors in which the function of charge carrier generation is separated from the charge carrier transport function. The layers are composed of a charge carrier generation layer (CGL) and a charge transport layer (CTL). The CGL contains charge carrier generation materials (CGMs) dispersed in polymers. The CTL is a solid solution of charge carrier transport materials (CTMs) in binder polymers. The combination of highly sensitive CGMs and high mobility CTMs enables improvement of the characteristics of

OPCs. Many companies developed new compounds which were commercialized in the 1980s.

After introducing organic photoreceptors for copiers in 1981, we have been developing many photoreceptors involving novel, improved materials. Figure 1 shows spectral sensitivities of various kinds of photoreceptors. It is shown that organic photoreceptors have surpassed the inorganic photoreceptors in sensitivities, especially in the wavelength region of laser diodes (780–800 nm). For laser diode printers, phthalocyanine pigments are commonly used as CGMs. A typical example is titanyloxy phthalocyanine (TiOPc). There are several crystal forms of TiOPc used for OPCs. Among them, D-form (Y-form) of TiOPc is suitable for high sensitivity OPCs used for laser printers.⁷ For analog copiers, azo pigments have been widely used, and the sensitivities of photoreceptors based on azo pigments have improved and become superior to those of inorganic photoreceptors, as shown in Fig. 1. The durability has also been improved remarkably. The lifetime of our first photoreceptor was only 10,000 copies. But in the 1990s, lifetimes of commercialized OPC drums 80 mm in diameter became greater than 300,000 copies. The lifetimes of larger OPC drums were much longer, thus useful for high speed copiers. These results indicate that organic materials are superior to inorganic ones when suitable materials and compositions are selected and used under appropriate conditions. There are many requirements for photoelectrical and mechanical properties of OPCs. For improving these properties, it is necessary to design and synthesize new materials and to optimize their composition by using both the new and known materials.

In this article, I describe our strategy for design and synthesis of azo pigments to improve the performance of OPCs.

Design of Novel Bisazo Pigments

The bisazo pigment is a popular CGM for copiers. A typical example is Chlorodiane Blue (CDB)⁶ shown in

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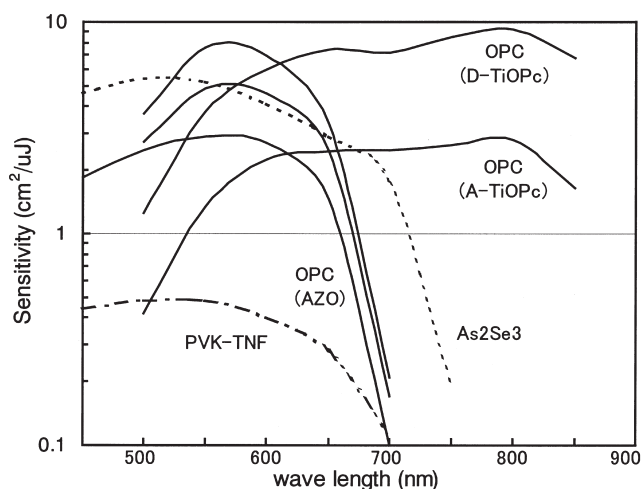
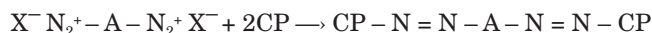


Figure 1. Spectral sensitivities of photoreceptors.

Fig. 2. Many new bisazo pigments have been developed for copiers and printers. Azo dyes are easily synthesized by the coupling reaction between diazonium salts of aromatic amines and coupling agents under mild alkaline conditions.

The characteristics of azo dyes depend on the combination of the aromatic amine (A) and the coupling agent or coupler (CP) moieties. Bisazo dyes are synthesized from tetrazonium salts of aromatic amines as shown below.



The characteristics of azo pigments are influenced by the molecular structures.

The combination of (A) and (CP) is very important. The sensitivity, spectral sensitivity and stability of OPCs are especially affected. It is important to elucidate the effect of molecular structure on the photoelectrical characteristic in order to improve performance of OPCs.

There are many couplers used for azo dyes. Figure 3 shows some examples. The popular ones are Naphthol AS, 2-Hydroxy-3-naphthoic acid anilide, (C-1) and its derivatives. Aromatic amines used for synthesis of tetrazonium salts are aniline derivatives and amino substituted polycyclic aromatic compounds. So many aniline derivatives can be designed by introducing various connecting moieties. We choose 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole as a starting material for preparing azo pigments. Tetrafluoroborate (BF_4^-) anion is usually used as the counterion (X^-). Coupling reactions are usually carried out in polar aprotic solvents such as DMF and DMSO. These solvents are useful for removing impurities. Washing with water and organic solvents are also important means for purification.

Our first bisazo pigment candidate for CGM was (A-1) shown in Fig. 4. But the photoreceptor using this azo pigment is poor in cyclic stability due to light fatigue. The coupler (C-2) has been developed for textile red monoazo dyes. A bisazo pigment (A-2) using this coupler (C-2) showed improved cyclic stability. The stability was also improved by optimizing the compositions and (A-2) was used in our first commercialized photoreceptor sheet for copiers. The lifetime of this sheet was 10,000 copies.

To improve the lifetime, we developed a novel coupler. Perinone pigments are well known to have good lightfastness. We characterized them as CGMs and con-

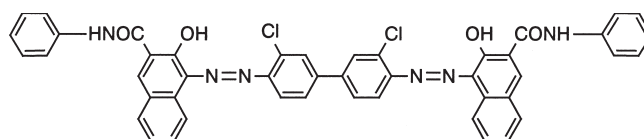


Figure 2. Chlorodiane Blue (CDB).

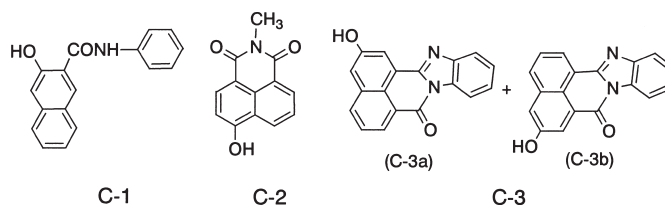


Figure 3. Typical coupling agents for azo pigments.

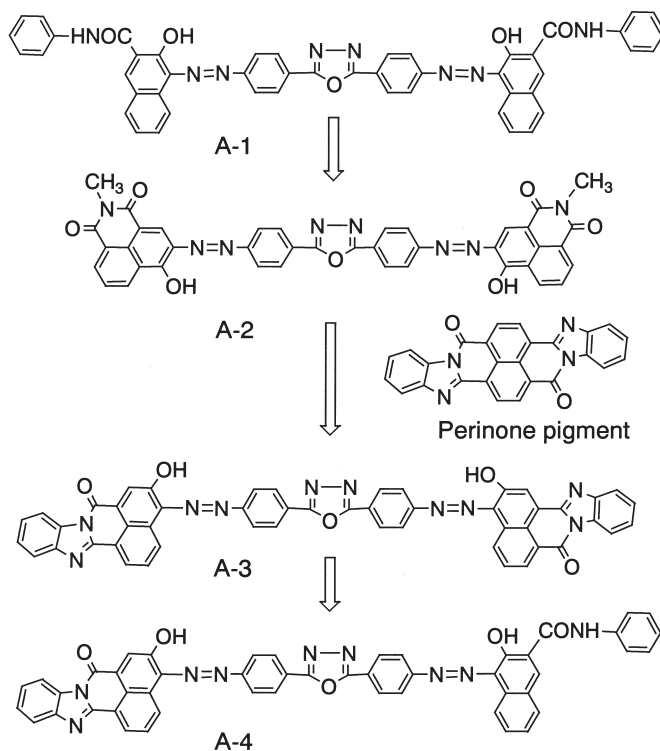


Figure 4. Design of azo pigments for improving characteristics of photoreceptors.

firmed their light stability in photoreceptors. We designed a new coupler having a moiety of the molecular structure of the light stable perinone pigment, and accordingly synthesized a novel coupler (C-3). We called it a "hydroxyperinone" coupler. This coupler is obtained by the reaction of 3-hydroxy-1,8-naphthalic anhydride and 1,2-phenylenediamine.⁸ The coupler is obtained as a mixture of two isomers, 2- and 5-hydroxy-7H-benz[de]benzimidazo[2,1-a]isoquinoline-7-one, (C-3a and C-3b). The bisazo pigment (A-3) was synthesized from this new coupler. The electrophotographic characteristics and cyclic stability of photoreceptors using this novel bisazo pigment (A-3) were much improved.⁸⁻¹⁰ Figure 5 shows the structures of three isomers of the bisazo pigment (A-3) synthesized from the isomeric mixtures of the coupler (C-3). The two isomers of the coupler (C-

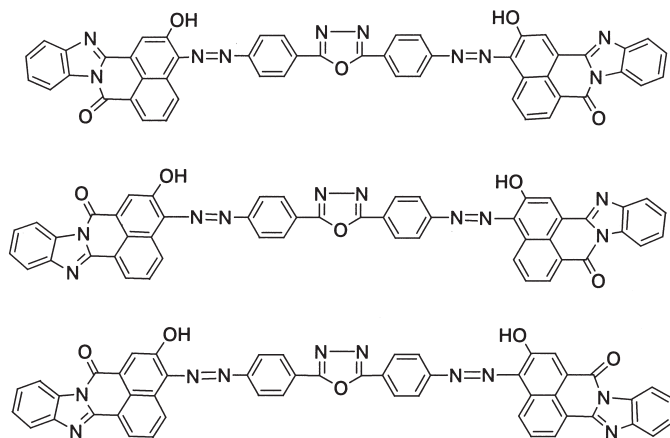


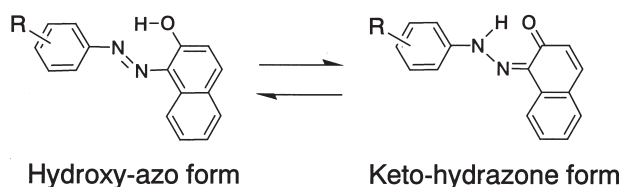
Figure 5. Isomers of bisazo pigment (A-3).

3) are obtained in almost equal amounts and can be separated by recrystallization with DMF. Each isomer of A-3 was prepared with separated isomers (C-3a and C-3b). The two isomers of (A-3) prepared by using of separated isomers (C-3a and C-3b) are similar in characteristics to the bisazo pigment (A-3) synthesized with mixed isomers of (C-3).¹⁰ So, the molecular structure of only one isomer is used to represent the bisazo pigment (A-3) in Fig. 4 and other figures.

Sensitivity and cyclic stability data of photoreceptors using three bisazo pigments mentioned above are shown in Table I. It is clear that the bisazo pigment (A-3) is the most stable CGM. Figure 6 shows charge acceptance of the photoreceptors having these bisazo pigments and CDB versus fluorescent lamp exposure time to examine light fatigue of the CGMs. The result shows that (A-3) is the most light stable, too. It is obvious that the hydroxyperinone coupler (C-3) is effective for improving characteristics of the bisazo pigment (A3). But, the basis for the structural effect of the hydroxyperinone coupler is not clear.

Tautomerism

It is well known that azo compounds synthesized from hydroxy substituted couplers may exist in two tautomers, hydroxy-azo and keto-hydrazone forms as shown in Scheme 1.¹¹ The elucidation of the tautomeric structure of the azo pigments used as CGMs in the solid state is very important in order to find the relationship between the molecular structure and the imaging characteristics. The existence of various tautomers has been observed and confirmed by IR, Raman, UV-VIS, NMR spectral analysis, X-ray structure analysis and other methods. Azo pigments containing Naphthol AS were studied to elucidate the tautomerism in the solid state by visible absorption spectral analysis. It was found that the keto-hydrazone form was dominant in every pigment.¹²



Scheme 1

TABLE I. Sensitivity and Cyclic Stability to Charge Acceptance of Bisazo Pigment-Based Photoreceptors Mentioned in Fig. 6. Half Decay Exposure is Measured as Sensitivity

	Sensitivity (Half-decay exposure)	Relative charge acceptance after 100 cycles
A-1	4.4 lux.sec	46 %
A-2	1.9	75
A-3	1.5	97

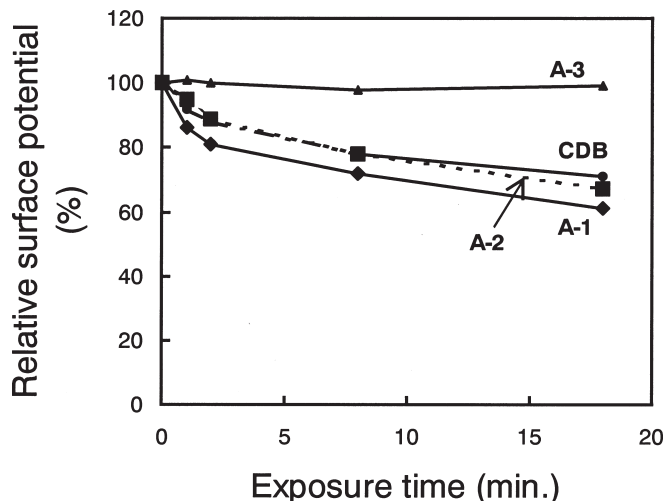


Figure 6. Light exposure effect on the charge acceptance of dual-layered photoreceptors using bisazo pigments. The photoreceptor has a CGL with a thickness of 0.4 μm containing 50 wt% bisazo pigment dispersed in polyvinylbutyral and a CTL with a thickness of 20 μm consisting of 50 wt% hydrazone (H-2), shown in Fig. 11 doped in polycarbonate. The light source is a fluorescent lamp covered with a cutoff filter (SC-540) for preventing from light absorption by the CTL. Light intensity is 750 $\mu\text{W}/\text{cm}^2$.

To study the tautomerism of azo pigments in the solid state, ¹³C NMR is a very useful method. The solid state ¹³C NMR spectra of monoazo¹³ and bisazo¹⁴ compounds synthesized using Naphthol AS derivatives were studied. In each case, the chemical shift at 170–180 ppm was observed and assigned to ketone carbonyl carbon. The chemical shift of hydroxy substituted carbon was not observed. These data show that azo compounds synthesized from Naphthol AS derivatives also exist in keto-hydrazone forms rather than hydroxy-azo forms in the solid state. Almost the same results are obtained by X-ray crystal structure analysis.¹⁵ The inter- and intramolecular hydrogen bonds are considered to contribute to the stabilization of the keto-hydrazone tautomers¹⁴ and to the sensitivity.¹⁶

Griffiths and Hawkins¹⁷ proposed a photofading mechanism in which singlet oxygen attacks the hydrazone form of azo compounds. This suggests that the cyclic stability and the light fatigue of photoreceptors shown in Table I and Fig. 6 may be attributed to the difference of the tautomeric forms of azo pigments used. We studied tautomerism of the bisazo pigments (A-1), (A-2) and (A-3) by ¹³C NMR spectroscopy to elucidate the structural effect on the light stability.¹⁸ The ¹³C NMR spectra of azo pigments (A-1), (A-2), (A-3), and (A-4) in the solid state are shown in Fig. 7. The chemical shifts at 170–180 ppm were assigned to ketone carbo-

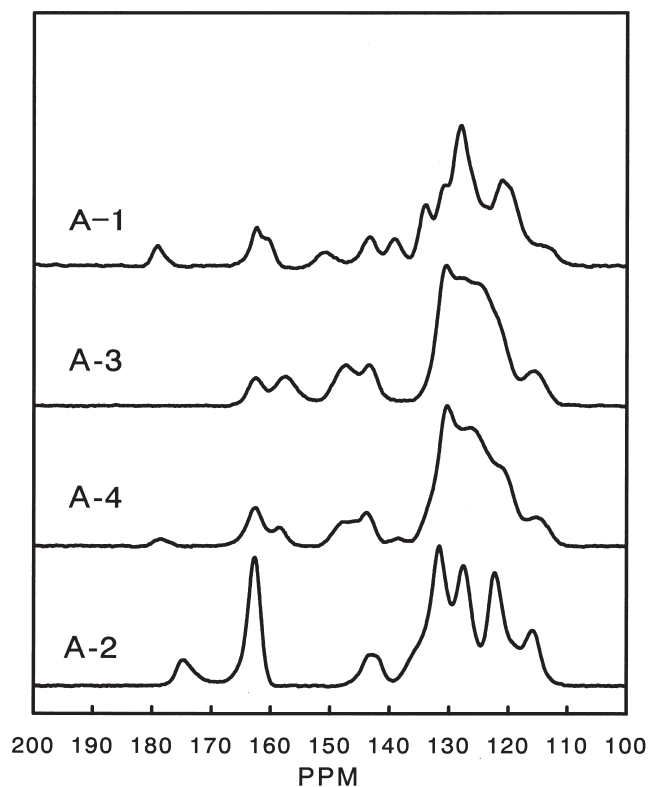


Figure 7. ^{13}C NMR spectra of bisazo pigments shown in Fig. 4 in the solid state.

nyl carbon.^{13,14} The peaks at 150 – 170 ppm were assigned to amide carbonyl carbon and hydroxy substituted aromatic carbon by comparing the spectral data of couplers shown in Table III and Table IV in the Experimental section and the literature data.¹⁴ The assigned spectral peaks are shown in Table II. The chemical shift data in Table II indicate that the bisazo pigments (A-1) and (A-2) are the keto-hydrazone forms and the bisazo pigments (A-3) is the hydroxy-azo form. The spectrum of bisazo pigment (A-4) shows the existence of both forms. These results are interpreted that the structure of coupling moiety affects the dominant tautomeric forms in the solid state. These data also indicate that the light stability of the unsymmetrical bisazo pigment (A-3) synthesized from the hydroxyperinone coupler is associated with the hydroxyazo form.

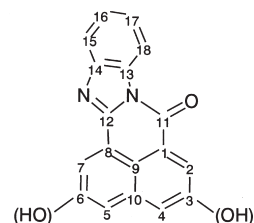
It has been reported that the dominant tautomeric form is influenced by the molecular structure of the azo moiety. It has been pointed out that an electron donor substituted aryl azo moiety stabilizes the hydroxy-azotautomer.¹⁹ The results of the absorption spectroscopic study of azo dyes show that *ortho*-substituents on naphthol couplers stabilized the keto-hydrazone tautomer by intramolecular hydrogen bonding to the carbonyl group of the keto form as shown in Fig. 8.²⁰

The electronic substituent effect may also affect the tautomeric equilibrium. Most bisazo pigments used as CGMs are Naphtol AS derivatives-based azo molecules having *ortho*-substituents. The bisazo pigment (A-2) has a coupler component with a *para*-imide carbonyl group. The hydroxyperinone coupler (C-3) has no *ortho*-substituents which could stabilize the keto-hydrazone tautomer by intramolecular hydrogen bonding. An *ortho*- or *para*-substituted electron-attracting group may also enhance

TABLE II. ^{13}C NMR Peak Assignments for Azo Pigments

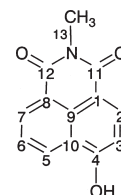
Type of carbon	A-1	A-2	A-3	A-4
C–OH	—	—	157.5	158.7
C=O(amide)	162.4	162.7	162.6	162.6
C=O(ketone)	179.1	174.7	—	178.6

TABLE III. ^{13}C NMR Peak Assignments for Hydroxyperinone Coupler (C-3)



Carbon No.	Chemical shift (ppm from TMS) (in DMSO)		
	C-3a	C-3b	(in Solid)
1	126.3	126.7	
2	127.1	112.6	
3	128.3	156.8 (C–OH)	156.5
4	121.8	116.0	
5	115.8	128.0	
6	156.0 (C–OH)	127.5	156.5
7	113.6	125.8	
8	130.0	130.6	
9	111.2	122.6	
10	127.1	131.0	
11 (C=O)	153.2	152.3	159.0
12 (C=N)	133.7	134.2	148.2
13	138.0	138.0	
14	148.8	148.8	140.5
15	120.5	120.5	
16	127.5	127.5	
17	121.7	121.7	
18	115.4	115.4	

TABLE IV. ^{13}C NMR Peak Assignments for Coupler (C-2)



Carbon No.	Chemical shift (ppm from TMS)	
	(in DMSO)	(in Solid)
1	120.9	
2	135.8	134.5
3	108.9	
4 (C–OH)	162.8	160.1
5	130.4	
6	123.6	
7	130.6	
8	120.1	
9	123.2	
10	120.6	
11 (C=O)	164.1	162.9
12 (C=O)	164.4	165.7
13 (CH ₃)	27.3	

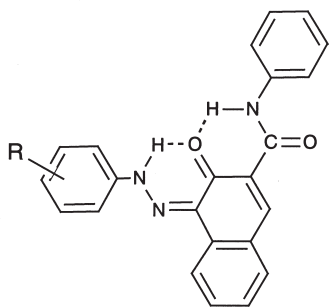


Figure 8. Intramolecular hydrogen bonding in the keto-hydrazone form.

proton transfer from the hydroxy group to the azo moiety, which further stabilizes the keto-hydrazone tautomer. The keto-hydrazone form of the bisazo pigment (A-2) may be attributed to the electronic substituent effect.

The hydroxyperinone coupler (C-3) also has electron-attracting carbonyl and imino groups, but they are substituted *meta* to the hydroxy groups. Therefore, there should be only minor substituent effects to stabilize the keto-hydrazone tautomer in the hydroxyperinone moiety, which results in the bisazo pigment (A-3) existing in the dominant hydroxy-azo form. From these data the superior stability of OPCs having the bisazo pigment (A-3) is attributed to the presence of the hydroxy-azo form in the solid state.

Unsymmetrical Azo Pigments

The performance of OPCs was rapidly improved in the 1980s. For design of highly sensitive azo pigments, we studied charge carrier generation phenomena in CGL having azo pigments. Phthalocyanines and azo pigments show different phenomena in the charge carrier generation process. It has been suggested that the charge carrier generation in CuPc occurs via an extrinsic process involving adsorbed O_2 .^{21,22} In the case of azo pigments, Umeda et al suggested that photo-excited azo molecules and CTMs on the surface of the azo particle interact and generate free carriers.^{23,24} The sensitivity of the photoreceptor mainly depends on the performance of CGMs; the combination of a CGM and a CTM also affects the sensitivity. The low ionization potential or oxidation potential for CTMs is effective in enhancing the photoinjection efficiency for holes. The substituent effect on the photoinjection efficiency of the pyrazoline-based photoconductors was measured. The electron donating substituents increased the injection efficiency.²⁵ But, in the case of hydrazone CTMs having different molecular structures, the photoinjection efficiencies of azo pigment-based OPC depend on the mobility rather than the oxidation potential of hydrazone CTMs.²⁶ The photoinjection efficiency of azo pigments shows different dependence on electric field and CTM, in contrast to phthalocyanine pigments.²⁷ The sensitivity of an azo pigment-based OPC without CTM is very low compared to the OPC containing CTMs.²⁸ These phenomena support the model that azo pigments generate charge carriers in conjunction with CTMs.^{24,25}

Figure 9 shows a photocarrier generation process model. A photoexcited azo molecule (exciton) and an adsorbed CTM on the surface of the pigment form an excited charge transfer complex (exciplex) leading to an

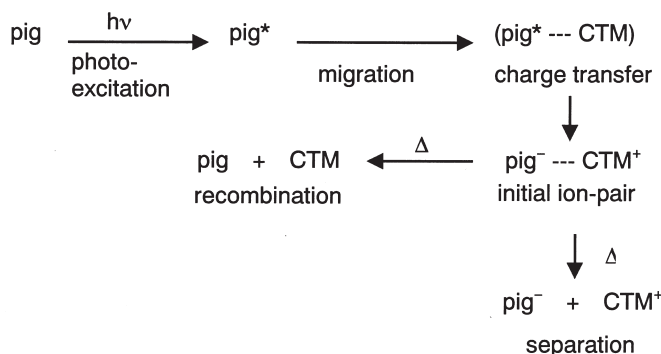
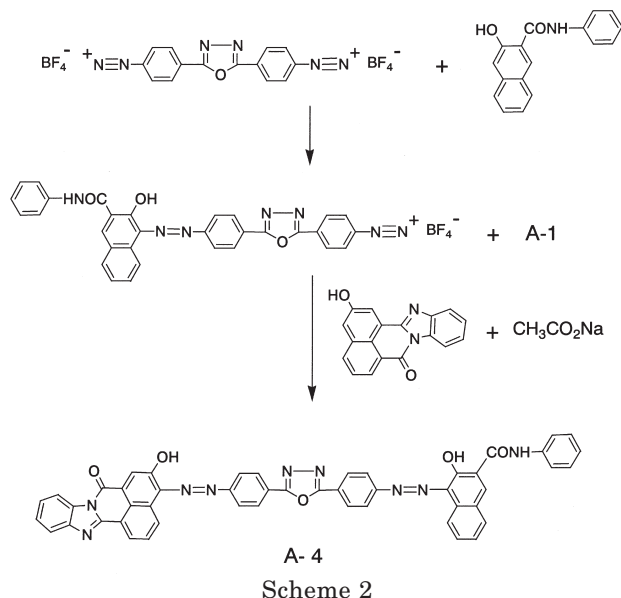


Figure 9. Mechanism of photocarrier generation in azo pigment-based photoconductors, where Δ stands for thermal energy.

ion pair. The ion pair separates into free carriers under applied electric field. In this model, if the exciton is highly polarized, such polarization is expected to be favorable to the excited state charge transfer process generating ion pairs. We performed Pariser–Parr–Pople molecular orbital (PPP MO) calculations to estimate the dipole moments in the first excited state (π – π^*) of various kinds of azo molecules to find a novel azo molecule having high polarization in the excited state. Most known bisazo pigments are symmetrical molecules and consist of the same two coupler moieties, which is unfavorable to high polarization. We designed various kinds of unsymmetrical azo molecules and estimated dipole moments in the excited states of these azo molecules. At the same time we synthesized these azo molecules and measured the sensitivities. We obtained a novel unsymmetrical bisazo pigment (A-4) shown in Fig. 4 with high sensitivity.^{28,29} The calculated dipole moment in the excited state of (A-4) was 19.5 D. The dipole moment in the excited state of (A-4) was also estimated by the electronic absorption spectrum method and came out about 15 D.³⁰ The photoreceptors using the novel unsymmetrical bisazo pigment (A-4) have provided useful high speed copiers.

The synthesis of this unsymmetrical bisazo pigment was described previously.²⁹ We found that the diazonium salts react with Naphthol AS (C-1) in DMSO solution without added base, while they do not react with the hydroxyperinone coupler (C-3) without base. This difference in reactivity is useful for synthesizing high purity unsymmetrical bisazo pigment (A-4) by controlling the reaction conditions. The coupling reaction can be carried out step by step by controlling the addition of base. An example of such a reaction is shown in Scheme 2. In this procedure, unreacted tetrazonium salt and intermediate by-product, (A-1), can be removed by filtration, respectively.

We tried to elucidate the mechanism of photocarrier generation to get more information on the factors contributing to high sensitivity. Measurement of thermally stimulated current (TSC)³¹ is useful for study of photocarrier generation phenomena in a dual layered OPC based on an azo pigment as a CGM. Using the TSC technique, we observed that the carrier generation efficiency of OPCs based on azo pigments showed very small dependence on temperature and electric field at low temperature (< 160 K).^{32,33} As shown in Fig. 9, it is suggested that the photoexcited state (or exciton) of an azo molecule migrates to the surface of the azo pigment particle and interacts with a CTM there to form an initial ion pair. This initial process is interpreted to reflect only



a small dependence on temperature and electric field at low temperature. Then the ion pairs separate into free carriers or disappear by recombination.^{32–34} The applied electric field assists the ion pair separation and depresses the recombination. The sensitivity depends on the quantum yield of the initial ion pair formation and the yield of carrier separation.

Figure 10 shows the electric field dependence of the number of collected carriers generated from ion pairs formed by irradiation at 120 K. The structures of hydrazone CTMs used are shown in Fig. 11. The number of collected carriers saturates at high electric field, which is interpreted as corresponding to the number of ion pairs generated by irradiation. The recombination rate is thought to be negligible compared to the separation rate at the high electric field. Comparing curves of samples using the same CTM in Fig. 10. The number of ion pairs formed in the sample made from the unsymmetrical azo pigment (A-4) is much larger than that of the sample using azo pigment (A-3). This suggests that the sample made from the unsymmetrical azo pigment (A-4) has larger ion pair generation efficiency than in the case of the symmetrical azo pigment (A-3). From comparison between the samples using the same CGM, the samples using (H-2) show much larger values of the number of collected carriers than the samples using (H-1). The samples using (H-2) are higher in sensitivity than the samples using (H-1). From these results, we conclude that the sensitivity of the dual layered OPC using the combination of azo pigments and hydrazones should mainly depend on the generation efficiency of the ion pairs or excited charge transfer complexes between an azo molecule and a hydrazone molecule.

These results support the idea that an unsymmetrical azo molecule having a large dipole moment in the excited state is most suitable for highly sensitive azo pigments.

Conclusion

We have developed a light stable bisazo pigment for use as a CGM by use of a novel hydroxyperinone coupler. The excellent light stability is attributed to the hydroxyazo tautomer of the bisazo pigment in the solid state. We designed azo molecules having large dipole moment

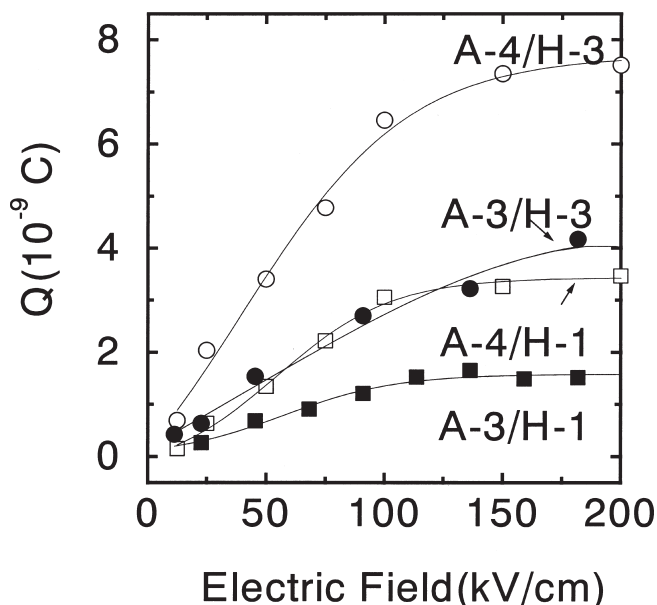


Figure 10. Field dependence of collected carriers (Q) with 120 K irradiation.

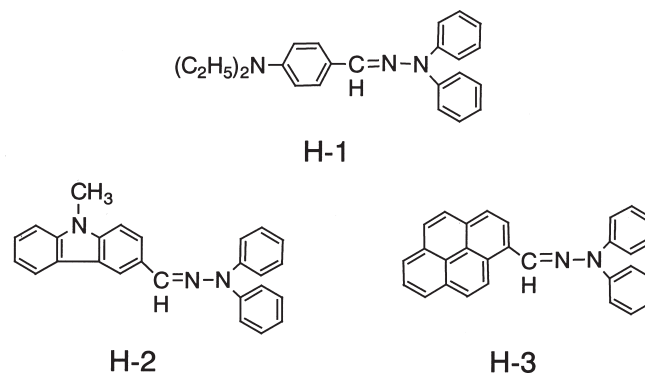


Figure 11. Some examples of hydrazones.

in the excited state and synthesized a highly sensitive unsymmetrical bisazo molecule containing a Naphthol AS coupler component and a hydroxyperinone coupler component. TSC measurements of the unsymmetrical bisazo pigment-based OPCs suggested that high generation efficiency of the initial ion pairs is a factor in the high sensitivity of this pigment.

Experimental Section

Materials were purchased or synthesized according to the methods described in the literature cited. Preparation of samples and methods of measurements are likewise described.

Solid state ^{13}C NMR spectra were obtained on a Bruker MSL-300 spectrometer operating at 75.47 MHz using ^1H - ^{13}C cross polarization, magic angle spinning, and total side band suppression. The solution ^1H and ^{13}C NMR spectra were measured on a Varian Unity Inova spectrometer at 500 and 125 MHz, respectively, in order to assign carbon atoms of couplers. The solution and solid state ^{13}C NMR spectral data for couplers (C-2) and (C-3) are shown in Table III and Table IV. ▲

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