

The Design of High Performance Organic Photoconductors

Tetsuo Murayama
Mitsubishi Chemical Corporation
MCC-Group Science & Technology Research Center
Yokohama, Japan

Abstract

We have studied the photogeneration and charge carrier transport processes in relation to the molecular structures of materials used in photoreceptors to elucidate the mechanisms of these phenomena. We applied the results to the design of photoconductive materials for improvement of performance and developed highly sensitive unsymmetrical azo pigments and new charge carrier transport materials with high mobility.

Introduction

Electrophotography is the key technology for copiers and laser printers. Inorganic photoconductors such as selenium alloys have been widely used for electrophotographic photoreceptors for many years. In 1970, IBM introduced the first organic photoconductor (OPC) for copiers. Since then, many companies have developed and commercialized OPCs for copiers and laser printers. Then, the inorganic photoconductors have been gradually replaced by OPCs. The OPCs have become dominant for electrophotographic photoreceptors with improvement of their characteristics.^{1,2}

The first organic photoreceptor used a single layered photoconductor based on poly-N-vinylcarbazole and 2,4,7-trinitrofluorenone (PVK/TNF).³ 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.^{4,5} They were dual layered organic photoconductors, and the functions of charge carrier generation and transport were separated into different layers. The charge carrier generation layer (CGL) contains charge carrier generation materials (CGMs) dispersed in polymers. The charge carrier transport layer (CTL) is a solid solution of charge carrier transport materials (CTMs) in polymers. The optimization of a CGL having a CGM with high efficiency of photogeneration and a CTL having a CTM with high mobility enables to get an OPC with improved characteristics. Many companies developed new compounds and commercialized organic photoreceptors using dual layered OPC in 1980s.

MCC introduced organic photoreceptors for copiers in 1981. We have been developing many photoreceptors with

improving the performance. Nowadays, we manufacture many types of organic photoreceptors with variety of sizes. They are used for analog and digital copiers, laser printers, color printers and plotters.

Figure 1 shows spectral sensitivities of various kinds of photoreceptors. It is shown that OPCs have surpassed the inorganic photoreceptors in sensitivity. The durability has also remarkably improved. The lifetime of our first photoreceptor was only 10k copies, but in 1990s, the lifetimes of commercialized OPC drums with a diameter of 80 mm became more than 300k copies. The lifetimes of larger OPC drums were much longer and used for high-speed copiers. These results show that organic materials are not inferior to inorganic ones when suitable materials and compositions are selected and used in appropriate conditions.

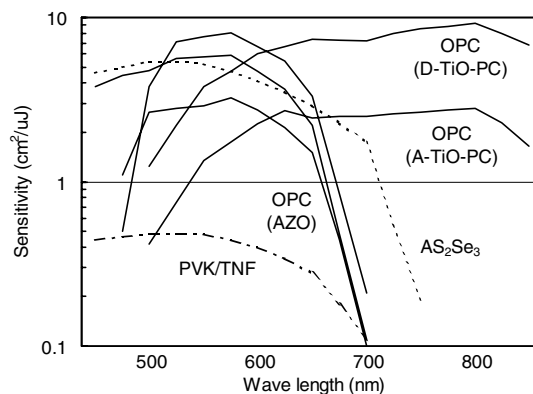


Figure 1. Spectral sensitivities of photoreceptors

Improvement of Photoreceptors

There are many factors and items to be considered in the design of photoreceptors. There are many requirements of photoelectrical and mechanical properties for OPCs. Developing photoconductive materials, polymers and additives, and optimizing their composition have improved photoelectrical and mechanical characteristics of organic photoreceptors.

In this paper, I describe some examples of molecular design of photoconductive materials to improve the performance of OPCs.

Design of Azo Pigments

We have developed and used two types of pigments as CGMs. Azo pigments are used for analog copiers and titanyloxy phthalocyanines (TiO-PCs) are used for digital copiers and diode laser printers. The minute particles of these CGMs are dispersed in CGLs. Absorption spectra and quantum yields of charge generation of CGMs are greatly dependent on their crystal forms. We found a crystal form of TiO-PC with high sensitivity. Figure 1 shows the spectral sensitivities of OPCs using two crystal forms of TiOPC. It is important to find crystal forms with good characteristics. But, it is difficult to design and synthesize suitable crystal forms of phthalocyanines with desired sensitivity. So, in this paper, some examples of design and synthesis of azo pigments are described.

We have used two kinds of disazo pigments for analog copiers, one is a symmetrical bisazo pigment and the other is an unsymmetrical disazo pigment. Azo dyes are easily synthesized by coupling reaction between diazonium salts of aromatic amines and coupling agents under the basic condition. The characteristics of azo dyes are dependent on the combination of the moieties of aromatic amine (A) and coupling agent (CP).



We selected diphenyloxadiazo unit as (A) after testing many diazonium salts of aromatic amines. There are many coupling agents used for azo dyes. Figure 2 shows some examples. The most popular ones are Naphthol AS (C-1) and its derivatives.

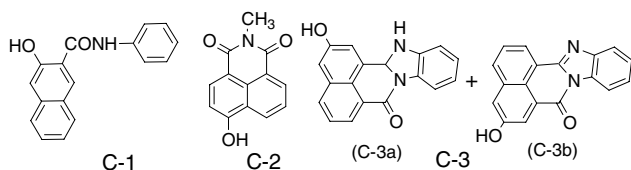


Figure 2. Some couplers

Our first bisazo pigment candidate for CGM was A-1 shown in Figure 3. But the photoreceptor using A-1 was poor in cyclic stability due to the light fatigue. A bisazo pigment (A-2) using C-2 was developed and used in our first commercialized photoreceptor sheet for copiers. The coupler (C-2) is MCC's original coupler developed for textile dyes. The lifetime of this sheet is 10k copies. To improve the lifetime, we designed and synthesized a novel coupler (C-3) which contains a moiety of molecular structure of light-stable perinone pigment shown in Figure 3. The bisazo pigment (A-3) was synthesized by using this

coupler. The electrophotographic characteristics and cyclic stability of OPC drums using A-3 were much improved.⁶

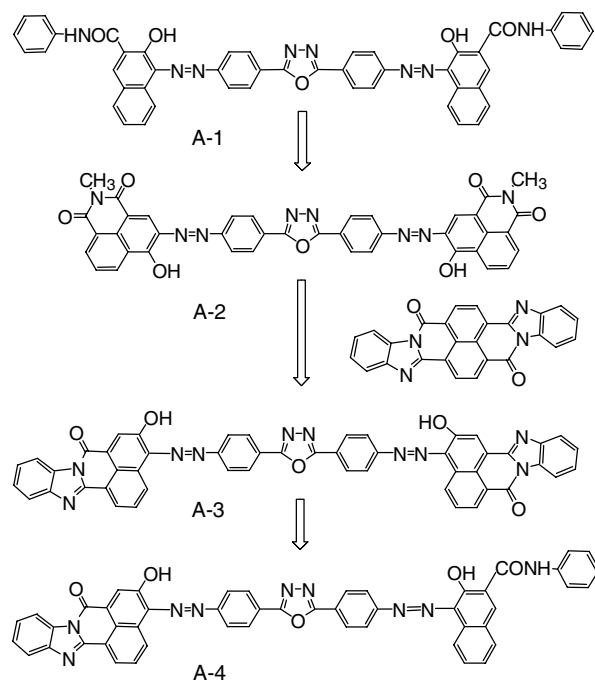


Figure 3. Improvement of Azo pigments

The coupler, C-3 is a mixture of two isomers, 2- and 5-Hydroxy-7H-benz[de]benzimidazo[2,1-a]isoquinoline-7-one, (C-3a and C-3b) and is called as hydroxyperinone coupler. The isomers of C-3 were synthesized in almost equal amounts and can be separated by recrystallization with DMF. The azo pigment A-3 has three isomers as shown in Figure 4. The characteristics of the isomers of A-3 synthesized with C-3a or C-3b are similar. So, we show one molecular structure of isomers of A-3 and other pigments having hydroxyperinone units in Figures.

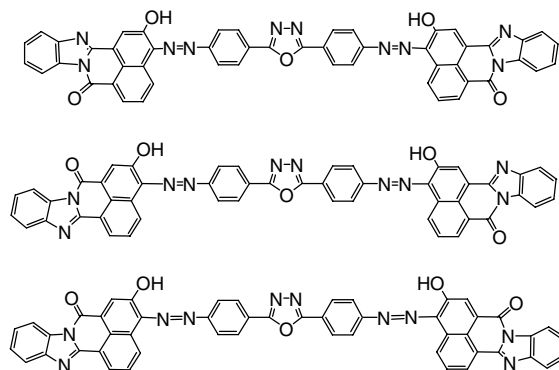
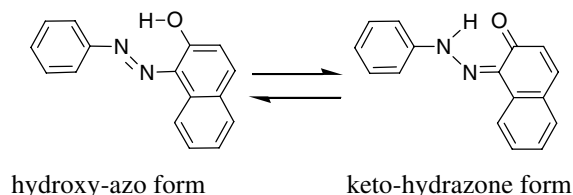


Figure 4. Isomers of bisazo pigment (A-3)

The effect of couplers on cyclic stability and light fatigue of OPCs using azo pigments have been studied. It is well known that azo-hydrazone tautomerism exists in azo dyes, hydroxy-azo and keto-hydrazone forms. The oxidative photofading of azo dyes is attributed to the photooxidation of keto-hydrazone forms.⁷ ¹³C NMR spectral data of azo pigments in solid state show that azo pigments A-1 and A-2 are keto-hydrazone forms but A-3 is hydroxy-azo form. Comparing the photofading data, it is suggested that tautomerism is an important factor for the light-stability of A-3.⁸



Highly Sensitive Azo Pigment

The performance of OPC was rapidly improved in 1980s. The requirement of highly sensitive azo pigment for high-speed copiers increased. For design of highly sensitive azo pigments, we studied charge carrier generation phenomena in CGL having azo pigments. There are many different phenomena in charge carrier generation process between phthalocyanine and azo pigments. The dual layered OPC having azo pigment shows sensitivity, but without the CTL it shows very low sensitivity. In dual layered OPC, photoinjection efficiency of azo pigments shows different dependence on electric field and CTM in contrast with that of phthalocyanine pigments.⁹ These phenomena suggest that azo pigments generate charge carriers with CTMs in the following model. A photo-excited azo molecule and an adsorbed CTM form an excited charge transfer complex (exciplex) and then an ion pair. The ion pair is separated into free carriers under the applied electric field. In this model, an azo molecule is needed to have large dipole moment in the excited state to form an ion pair easily. The bisazo pigment is a symmetrical molecule and it is unfavorable for having large dipole moment. To get large dipole moment, we designed various kinds of unsymmetrical azo molecules and estimated dipole moments in the excited states of these azo molecules by using of molecular orbital calculations. At the same time we synthesized these azo molecules and observed the sensitivities, and we got a novel unsymmetrical disazo pigment (A-4) with high sensitivity.¹⁰ We measured the dipole moment in excited state of A-4 by using electroabsorption method and got a large value of about 15 Debye. The unsymmetrical disazo pigment (A-4) has been used in photoreceptors for high-speed copiers.

We measured thermally stimulated currents (TSC)¹¹ to elucidate the charge carrier generation process in dual layered photoconductors based on azo pigments and

hydrazone compounds. Figure 5 shows that the collected carrier (Q) of the sample using unsymmetrical azo pigment (A-4) is much larger than that of the sample using symmetrical azo pigment (A-3). The hydrazone compounds also affect the value of Q. These results suggest that the sensitivities of azo pigment based layered OPC depend on the generation efficiencies of the ion pairs between the azo molecules and hydrazone compounds. We also observed time-resolved fluorescence spectra of azo pigments to elucidate factors for high sensitivity.¹²

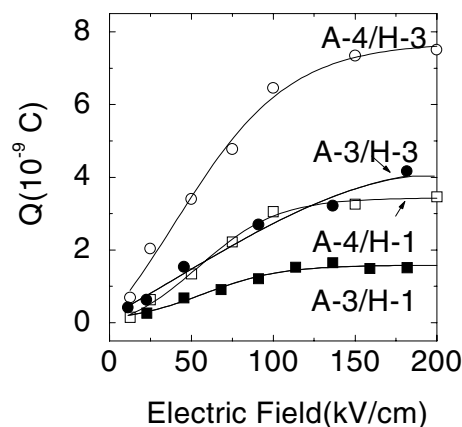


Figure 5. The field dependence of collected carrier (Q) at 120K irradiation temperature.

Design of CTM

The CTL transports the charge carriers generated in the CGL and reduces the surface potential to the required level. The CTL is required many photoelectrical and mechanical functions. They are high charge acceptance, low dark decay, high carrier injection efficiency, high carrier mobility, transparency to exposure light, abrasion resistance, environmental resistance and so on. Some of them are affected by the characteristics of the CGL but the properties of CTLs are important. Most of the CTLs consist of solid solutions of CTMs and polymers. Many CTMs are electron-donating compounds and transport holes.

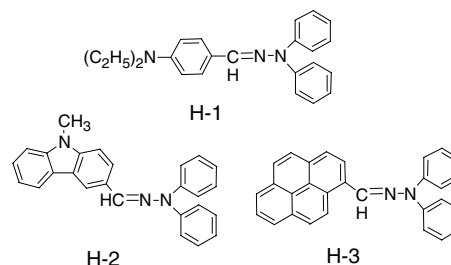


Figure 6. Some examples of hydrazone compounds.

We have developed hydrazone compounds for CTMs. Hydrazone compounds are readily synthesized from

aromatic aldehydes. We designed and synthesized many hydrazone compounds derived from aldehydes of aromatic hydrocarbons and aromatic heterocyclic compounds. The examples are H-2 and H-3 shown in Figure 6.

Hole transport process is an electron transfer reaction from a neutral molecule to a cation radical of transport molecule in the CTL. Therefore, ionization potential or oxidation potential of the molecule is an important factor for mobility of a CTM. But when we measured mobilities of some hydrazone compounds, we got no good correlation between mobilities and oxidation potentials. The results suggested that the effect of molecular orientation and overlapping is also important for the mobility.^{13,14} For the design of improved CTMs with high mobility, we have tried to elucidate the effect of molecular structure and molecular properties of CTMs on the mobility by using computational analysis and we got a guideline for design of high mobility CTMs.

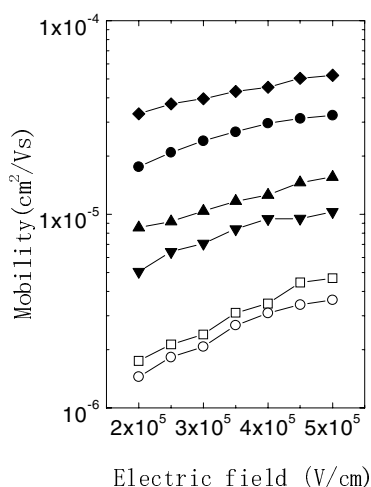


Figure 7. Hole drift mobility of some CTMs in polycarbonate (50wt%)

We designed several hydrazone compounds with large polarizability and small dipole moment, and measured high mobility.¹⁵ This guideline is applied to the design of arylamine derivatives and we synthesized novel arylamine compounds with very high mobility shown in Figure 7. These new CTMs contribute to design high performance OPC.

The characteristics of photoconductive materials and the performance of OPC have been much improved during these three decades. The application and the market of OPC have expanded surprisingly. Continuing the studies to elucidate the phenomena and mechanism of

electrophotographic processes will contribute the further improvement of OPC.

Acknowledgements

The Author would like to express his thanks to his colleagues at Mitsubishi Chemical Corp., especially Shigenori Otsuka, Hitoshi Ono, Shinji Aramaki, Takayuki Shoda and Mamoru Nozomi for their support, experimental work and helpful discussions.

References

1. Kock-Yee Law, *Chem. Rev.*, **93**, 449 (1993)
2. Paul M. Borsenberger and David S. Weiss, *Organic Photoreceptors for Xerography*, Merce Dekker, NY, 1998.
3. R. M. Shaffert, *IBM J. Res. Develop.*, **15**, 75 (1971).
4. P.J. Melz, R.B. Champ, L.S. Chang, C. Chiou, G.S. Keller, L.C. Licican, R.R. Neiman, M.D. Shattuck, W.J. Weiche, *Photo. Sci. Eng.*, **21**, 73 (1977).
5. E-G. Schlosser, *J. Appl. Photo. Eng.*, **4**, 118 (1978).
6. Shigenori Otsuka, Tetsuo Murayama and Hideki Nagasaka, *Proc. NIP 3*, pg.16. (1986).
7. John Griffiths, Christopher Hawkins, *J. Chem. Soc.*, 747 (1977).
8. Hitoshi Ono, Iwao Takagishi, Eri Matsuda and Tetsuo Murayama, *Proc. NIP6*, pg.312 (1990).
9. Mamoru Nozomi, Itaru Ogawa, Shinji Aramaki and Shigenori Otsuka, *Proc. NIP5*, pg.17 (1989).
10. Osamu Murakami, Toru Uenaka, Shigenori Otsuka, Shinji Aramaki and Tetsuo Murayama, *Proc. NIP7*, pg.318 (1991).
11. Takayuki Shoda, Shinji Aramaki and Tetsuo Murayama, *Proc. NIP 14*, pg. 508. (1998).
12. Yutaka Sasaki, Shoichi Yamaguchi, Takayuki Shoda, Shinji Aramaki and Tetsuo Murayama, *NIP17*, (2001).
13. Tetsuo Murayama, Sshinji Aramaki, Takao Matsuzaki and Tomoko Ito, *Proc. NIP4*, pg.15 (1988).
14. Akiteru Fujii, Takayuki, Shoda, Shinji Aramaki and Tetsuo Murayama, *Jpn. J. Appl. Phys.*, **36**, 2739 (1997).
15. Takayuki Shoda, Akiteru Fujii, Tetsuo Murayama and Shinji Aramaki, *Proc. NIP15*, pg. 651 (1999).

Biography

Tetsuo Murayama received his B.S., M.S., and D.S. degrees in Chemistry from the University of Tokyo in 1965, 1967 and 1970 respectively. Since 1970 he has worked in Yokohama Research Center at Mitsubishi Chemical Corporation, where he started to study OPC. His research interests are in molecular design and physical organic chemistry of OPC, functional dyes and related aromatic compounds. Currently he is a Fellow and works in MCC-Group Science & Technology Research Center at MCC in Yokohama. He is a member of the IS&T and the ISJ.