Dyes and Pigments **9** (1988) 343–350

Syntheses and Absorption Spectra of Intermolecular Charge-Transfer Complex Dyes

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(Received 14 September 1987; accepted 27 October 1987)

ABSTRACT

The intermolecular charge-transfer (CT) complexes derived from carbazoles as donors and naphthoquinones as acceptors were evaluated as coloring matter. The synthetic design of CT complex dyes from the point of view of their absorption spectra was carried out by means of the PPP MO method.

Dyes absorbing light in the region from the visible to the near-infrared wavelengths were synthesised. Their spectral characteristics were correlated with donor–acceptor characteristics and with chemical structures. Good linear correlations were observed between the calculated and the observed values of the first excitation energy. Some applications of CT dyes for color former and optical recording media are discussed.

1 INTRODUCTION

There is a current interest in the development of new dyes for use as functional materials in electronic and optoelectronic devices. There are many chromophores which show intramolecular charge-transfer absorption spectra, but few are known with respect to intermolecular charge-transfer chromophores which are used practically as coloring matter.

Intermolecular charge-transfer (CT) complexes have been studied for use as organic electronic conductors (OECs) and organic photoconductors (OPCs). Thus, a tetrathiafulvalene (TTF)–tetracyanoquinodimethane (TCNQ) intermolecular CT complex has been examined as an OEC,[1,2] and better combinations of stronger donors and acceptors have been studied in

Dyes and Pigments 0143-7208/88/$03·50

the context of organic metals.[3] On the other hand, the poly-*N*-vinylcarbazole (PVCz)–2,4,7-trinitrofluorenone (TNF) intermolecular CT complex has been examined as an OPC for electrophotography.[4,5] New types of intermolecular CT complexes are thus anticipated not only as OECs or OPCs but also as coloring matter.

Spatz and Shackle[6] have reported some intermolecular CT complexes, such as the combination of polyalkylbenzenes and benzoquinones, for use as color formers but their spectral properties were not studied in detail.

The color and constitution of organic dyes can be evaluated quantitatively by means of the PPP MO calculation method[7,8] and their synthetic design with respect to their absorption spectra can be readily effected.[9]

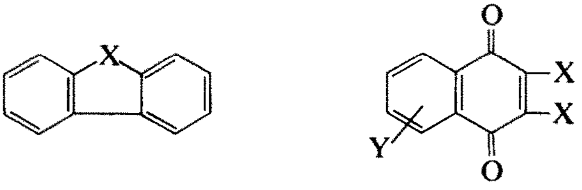
In this present paper, a new synthetic design of intermolecular CT complex dyes using the PPP MO method has been described. Additionally, the syntheses and characteristics of some new carbazole–naphthoquinone CT complex dyes have been studied in detail.

2 RESULTS AND DISCUSSION

2.1 Synthetic design of intermolecular CT complex dyes by the PPP MO method

Carbazole analogues **1** and naphthoquinone derivatives **2** were used as donors and acceptors, respectively. Carbazole and its analogues are well known as electron donors and naphthoquinones as electron acceptors, but their combinations have not yet been examined as coloring matters.

It is well known that the absorption spectra of intramolecular charge-



1

a: X = NEt
b: X = NH
c: X = Se
d: X = S
e: X = O
f: PVCz

2

a: X = Cl, Y = H
b: X = H, Y = 5-NO_2
c: X = Cl, Y = 5-NO_2
d: X = Cl, Y = 6-NO_2
e: X = CN, Y = H
f: X = CN, Y = 5-NO_2
g: X = CN, Y = 6-NO_2
h: X = CN, Y = 5,7-di NO_2

Scheme 1

transfer dyes are affected largely by substituents of a donor and/or an acceptor nature. These effects are recognized by the differences between the energy levels of the HOMOs and LUMOs, and by the π-electron density changes accompanying the excitations. The absorption maximum of intermolecular CT dyes can also be determined in the same manner; excitation energy can be estimated as the energy difference between the LUMO of the acceptor and the HOMO of the donor, so that the first excitation energy can be obtained by the PPP MO method.

The energy levels of the donors ($\varepsilon_{\text{HOMO}}$) **1a**, **1b**, **1d** and **1e** were calculated to be −8·56, −8·78, −9·11 and −9·34 eV, respectively. The $\varepsilon_{\text{LUMO}}$ of the acceptors **2e**, **2f**, **2g** and **2h** were found to be −4·28, −4·64, −4·77 and −4·93 eV, respectively.

From these results it was shown that the electron-donating ability of the donors was affected by the ring hetero-atom of **1**. The strength of the donor decreased in the order **1a** > **1b** > **1d** > **1e**. In the case of the naphthoquinones **2**, the type and orientation of the substituent noticeably affected their electron-withdrawing ability, i.e. the more electron-withdrawing substituents (such as cyano or nitro groups) decreased the $\varepsilon_{\text{LUMO}}$, and the 6-nitro group was more effective than the 5-nitro group. Hence the strength of the acceptors decreased in the following order: **2h** > **2g** > **2f** > **2e**. The first excitation energy of intermolecular CT dyes, which was represented as ΔE_1, was easily obtained from the difference between $\varepsilon_{\text{LUMO}}$ and $\varepsilon_{\text{HOMO}}$.

The calculated first excitation energies (ΔE_1) and the observed values (ΔE_{max}) obtained from the absorption maximum of the CT dyes are summarized in Table 1, and ΔE_1 against ΔE_{max} is plotted in Fig. 1. It is noteworthy that a linear correlation is obtained from Fig. 1, and eqn (1) is correlated between ΔE_1 and ΔE_{max}. It was found that the λ_{max} of CT dyes can be calculated quantitatively, and the synthetic design of intermolecular CT

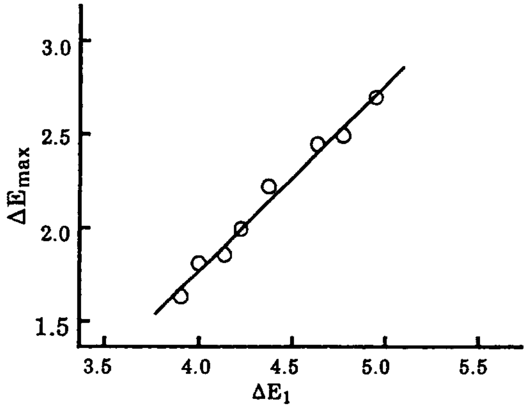


Fig. 1. Linear relationship between ΔE_1(calculated) and ΔE_{max}(observed).

TABLE 1
The Calculated (ΔE_1) and Observed CT Transition Energies (ΔE_{max}) of Combinations of Donors and Acceptors

		1a	**1b**	**1d**	**1e**
2e	ΔE_1 (eV)	4·08	4·30	4·63	4·86
	ΔE_{max} (eV)	1·79	2·03	2·37	2·61
2f	ΔE_1 (eV)	3·92	4·14	4·47	4·70
	ΔE_{max} (eV)	1·65	1·82	2·16	2·38
2g	ΔE_1 (eV)	3·79	4·01	4·34	4·57
2h	ΔE_1 (eV)	3·63	3·85	4·18	4·41

dyes can be achieved from their absorption spectra calculated by the PPP MO method.

$$\Delta E_1 \text{ (eV)} = -2{\cdot}352 + 1{\cdot}015 \times \Delta E_{max}\text{(eV)} \tag{1}$$

2.2 Syntheses and absorption spectra of intermolecular CT dyes

It was found that combinations of the donor **1** and the acceptor **2** gave various dyes absorbing light in the region from the visible to the near-infrared wavelengths. When the donor and the acceptor were mixed in solution, CT dyes were formed in the equilibrium mixture, but some of these CT dyes were precipitated. The λ_{max} and the color of the intermolecular CT dyes are summarized in Table 2, and the observed absorption spectra of the CT dyes obtained from various donors and 5-nitro-2,3-dicyano-1,4-naphthoquinone as an acceptor are shown in Fig. 2.

Broad absorption spectra, arising from overlapping of the first and second

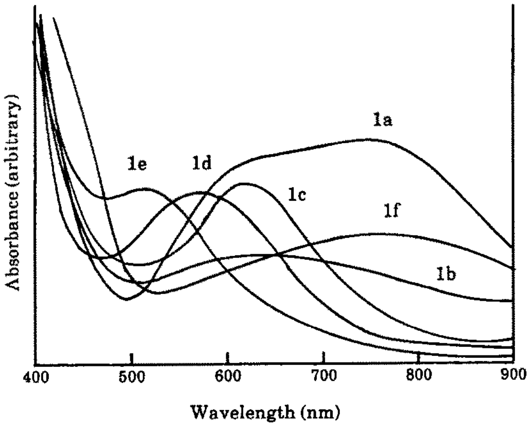


Fig. 2. The absorption spectra of intermolecular CT dyes (acceptor: 5-nitro-2,3-dicyanonaphthoquinone).

TABLE 2

The Absorption Maximum (nm) and Color of the Intermolecular CT Complex Dyes

	1a	**1b**	**1c**	**1d**	**1e**
2a	440 Yellow				
2b	512 Orange				
2c	535 Purple	498 Red	479 Orange	467 Orange	Yellow
2d	556 Purple		482 Orange		
2e	560–700 Green	550–650 Green	555 Purple	523 Red	475 Orange
2f	580–770 Green	570–700 Green	607 Dark blue	575 Blue	520 Red
TNF	560 Purple	518 Red		463 Orange	Yellow
TCNQ	588 Blue	518 Red		531 Purple	492 Red

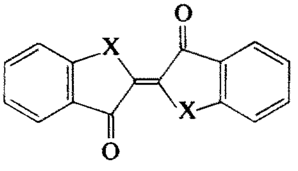
CT bands, are observed when carbazoles are used as the donors. The first and the second CT bands are considered to be due to the CT from the HOMO and NHOMO levels of the donor, respectively, to the LUMO level of the acceptor. These observations have been reported in the CT absorption spectra between carbazoles and tetracyanoethylene.[10]

The calculated absorption maximum was consistent with the observed value. The strength of the donor property was in the order **1a** > **1b** > **1c** > **1d** > **1e**. These tendencies of donor property were also observed in the indigo chromophores, in which the first transition arose from intramolecular CT character. The effects of hetero-atoms on the absorption maximum of both chromophores are shown in Table 3.

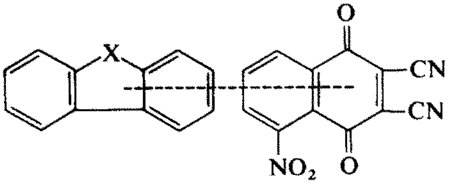
The electron-donating properties of hetero-atoms are of the same order in both cases. The electron-donating property of the selenium atom is stronger than that of the sulfur atom but weaker than that of the amino group, and it is possible to estimate the parameters of the selenium atom for the PPP MO calculation.

The strength of the acceptors can be decided in a similar manner and the results obtained corresponded well with the computed values. Substitution by the cyano group at the 2- and 3-positions of 1,4-naphthoquinone produced a 150–200 nm bathochromic shift of the CT band. Substitution by the nitro group at the 5- or 6-position also produced a 50–90 nm bathochromic shift, the 6-nitro group being more effective than the 5-nitro

TABLE 3
The Effect of Hetero-atoms on the λ_{max} of Indigoes and Intermolecular CT Complex Dyes



Indigo



CT dye

	$X=NEt$	$X=NH$	$X=Se$	$X=S$	$X=O$
Indigo	650	605	570	546	420
CT dye	740	640	607	575	520

group. These observations were quantitatively reproduced by the PPP MO calculation.

It is possible to estimate the electron-withdrawing ability of naphthoquinone acceptors from the λ_{max} of CT dyes examined here. 2,4,7-Trinitrofluorenone (TNF) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) are well known as acceptors, and their CT absorption maxima with **1a** were 560 nm (THF) and 588 nm (TCNQ), respectively. Comparing with the λ_{max} values of naphthoquinones as acceptors, the order **2e** (640 nm) > TCNQ (588 nm) > TNF (560 nm) > **2d** (556 nm) was obtained. It is suggested that the naphthoquinone derivative **2e** is a stronger acceptor than TCNQ or TNF. From these results it was concluded that the naphthoquinone derivatives act as the effective acceptors for deep-colored CT dyes.

2.3 Some applications of the intermolecular CT dyes

Whilst intermolecular CT complexes have been widely studied as OECs and OPCs, few have been reported as coloring matter. Some applications of CT dyes have been examined. Thus, the CT dyes obtained from **1a** or **1b** with **2f** absorb near-infrared light and are of interest in application for optical recording media for semiconductor lasers.[12]

When poly(*N*-vinylcarbazole), **1f** is used as the donor, the CT polymeric dyes can be obtained and used as coating agents to obtain thin layer film which can be used as a recording layer. The thin layer of polymeric dyes can be readily prepared by the dip coating method, and their absoprtion spectra are the same as those in the solution. It was found that these thin layer films were stable when irradiated by a xenon lamp for 10 h.

The CT dyes prepared from **1a** with some acceptors can be applied to heat-sensitive color former systems. The mixture of *N*-ethylcarbazole and naphthoquinones did not produce color in the solid state at room temperature but when the temperature was raised over 70°C, **1a** melted and the color was readily developed by the formation of CT dyes. This heat-sensitive color former system is very simple and no additive is necessary. Various colors, for example black, could be produced by changing the combinations of donors and acceptors.

Intermolecular CT dyes have many interesting properties and many applications can be proposed as well as their use for OECs and OPCs. Other applications of new types of naphthoquinone–carbazole CT complex dyes are now under investigation.

3 EXPERIMENTAL

All the melting points are uncorrected, and were measured using a Yamato MP-21. The absorption spectra were measured in dichloromethane at a concentration of 2×10^{-2} mol litre^{-1} using Shimazu UV-240 and UV-265 FS spectrophotometers. The IR spectra and ^{1}H-NMR spectra were measured using Shimazu IR-420 and JEOL JNM-NH-100 and JNM-GX-270, respectively. The mass spectra were recorded on a Shimazu LKB-9000 spectrometer operating at 80 eV. Elemental analyses were recorded using Yamato CHN recorder MT-3. Column chromatography was carried out on silica gel (Wako C-300) using an appropriate organic solvent as eluant. The PPP MO method was used with variable approximation. Configuration interaction was not considered in the system. Calculations were carried out as previously described.[9,11]

3.1 Materials

All donors, except **1c**, were of commercial grade. Acceptors were synthesized and purified by recrystallization following literature procedures.[13] Compounds **1c**, **2c**, **2d** and **2e** were synthesized as outlined below.

3.1.1 6-Nitro-2,3-dichloro-1,4-naphthoquinone (**2d**)

Compound **2d** was obtained by nitration of **2a** together with 5-nitro-2,3-dichloro-1,4-naphthoquinone **2c**, and was separated from **2c** by column chromatography using a mixture of benzene:*n*-hexane (1:1) as eluant. The 6-nitro isomer **2d** was obtained as the first fraction, followed by the 5-nitro isomer **2c**.

2c: m.p. 173°C; mass, M^+, 237; λ_{max} 344 nm (in MeCN).
2d: m.p. 181–182°C; mass, M^+, 237.
^{1}H-NMR, δ(ppm): 8·28(d, 1H), 8·48(d, d, 1H), 8·86(s, 1H).

3.1.2 2,3-Dicyano-1,4-naphthoquinone (**2e**)

Dicyanation of 2,3-dichloro-1,4-naphthoquinone, followed by oxidation, gave 2,3-dicyano-1,4-naphthoquinone (using a similar procedure to that for the preparation of **2f**) in 41·4% yield.

2e: m.p. 270°C.

3.1.3 Dibenzoselenophene (**1c**)

Dibenzoselenophene was synthesized from *o*-aminobiphenyl by McCullough's procedure.[14]

1c: m.p. 78°C.
Analysis: Found: C, 62·11; H, 3·29. Calcd: C, 62·29; H, 3·47%.

3.2 Synthesis of intermolecular charge-transfer dyes (general procedures)

The donor and acceptor were each dissolved in dichloromethane at a concentration of about $2 \times 10^{-2}\,\mathrm{mol\,litre^{-1}}$. After mixing of the two solutions, CT complex dyes were formed immediately. In some cases, for example **1d** and **2f**, a precipitate was obtained. After removal of the solvent, the CT dye could be isolated as solid crystals. The fine structure of the CT dyes was confirmed by X-ray diffraction; details will be reported separately.

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