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Yousuke Ooyama, Yuichiro Oda, Tomonobu Mizumo, Joji Ohshita

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Specific solvatochromism of D- π -A type pyridinium dyes bearing various counter anions in halogenated solvents

Yousuke Ooyama,* Yuichiro Oda, Tomonobu Mizumo, and Joji Ohshita**

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

Abstract— Donor- π -acceptor type pyridinium dyes **OD1–OD4** bearing various counter anions (X⁻ = Cl⁻, Br⁻, l⁻, or BPh₄⁻) have been designed and developed to gain greater insight into the influences of the electronic structures of D- π -A type pyridinium dye on the specific solvatochromism in halogenated solvents: the intramolecular charge transfer absorption bands of the dyes **OD1–OD4** in halogenated solvents show a large bathochromic shift compared with those in the non-halogenated solvents. This study revealed that the halogenated solvents can significantly enhance the intramolecular charge transfer characteristics of D- π -A type pyridinium dye with soft counter anion, leading to large bathochromic shift of absorption band in halogenated solvents, which is good agreement with an increase in the energy of halogen-halide anion interaction for the type of the halogen atom of halogenated solvents. © 2012 Elsevier Science. All rights reserved

Introduction

Solvatochromic dyes have received considerable attention over many years because of a fundamental interest in photochemistry and their application as environmental probes for determination of local polarity in macrosystems (e.g. membrances, polymers, and sol-gel matrices) and detection of volatile organic compounds.^{1–12} Among the various types of solvatochromic dyes, donor- π -acceptor (D- π -A) type pyridinium dyes having diphenyl or dialkyl amino group as electron donor and pyridinium ring as electron acceptor linked by a π -conjugated bridge, and bearing a halide anion as counter anion are known well to show negative solvatochromism (i.e., the dye shows a hypsochromic shift of the intramolecular charge-transfer (ICT) absorption band with increasing solvent polarity).^{13–30} Almost all chemists may understand that the negative solvatochromism would be ascribed to the change of the

solvatochromism would be ascribed to the change of the electronic ground-state structure of the pyridinium dye on changing of solvent polarity; with increasing solvent polarity the ground state is more stabilized than the excited state because the ground state is more dipolar than the excited state, and this produces a hypsochromic shift.^{1, 18, 19} In our previous study we have mentioned another interesting characteristic of D- π -A type pyridinium dyes is

that the bathochromic shifts of ICT absorption band in halogenated solvents such as dichloromethane and dibromomethane are larger than those in non-halogenated solvents of similar dielectric constant (ε_r) values.²⁴ The specific solvatochromism of dyes in halogenated solvents is also observed for neutral (non-ionic) D- π -A dyes having strong electron-withdrawing group.³¹ However, there have been few efforts to clarify the influences of halogenated solvent on the large bathochromic shifts, although the specific solvatochromism is of a great interest from an academic viewpoint, together with a practical importance such as development of sensors for halogenated organic compounds.³² Thus, recently, we investigated the specific solvatochromic behaviors of D- π -A type pyridinium dye bearing an iodide ion as the counter anion. It was found that the bathochromic shifts of ICT absorption band in iodinated solvents such as iodobenzene and diiodomethane are larger than those in chlorinated and brominated solvents.

In this study, to gain greater insight into the influences of the electronic structures of D- π -A type pyridinium dye on the specific solvatochromism in halogenated solvents, we have designed and synthesized D- π -A type pyridinium dyes **OD1–OD4** having diphenylamino group as an electron donor and pyridinium ring as an electron acceptor linked by carbazole as a π -conjugated bridge, and bearing various counter anions (X⁻ = Cl⁻, Br⁻, l⁻, or BPh₄⁻). The dyes **OD1–**

^{*} Corresponding authors. Tel.: +81 82 424 7689; fax: +81 82 424 5494; e-mail: yooyama@hiroshima-u.ac.jp (Y. Ooyama), jo@hiroshima-u.ac.jp (J. Ohshita)

OD4 showed the specific solvatochromism, leading to large bathochromic shift of ICT absorption band in halogenated solvents. Furthermore, it was found that bathochromic shifts of ICT absorption bands become larger in order of soft counter anion $CI^- < Br^- < I^- < BPh_4^-$. The influences of halogenated solvents on the large bathochromic shifts of ICT absorption band are studied on the basis of ¹H NMR measurements and theoretical calculations. Here we discuss the specific solvatochromism from the viewpoint of the enhanced ICT characteristics of the D- π -A pyridinium dyes in halogenated solvents.

Results and discussion

The D- π -A type pyridinium dyes **OD1–OD3** were prepared from diphenyl-[7-(5-pyridin-4-yl-thiophen-2-yl)-9*H*-carbazol-2-yl]-amine **1**³³ and the corresponding *n*-butyl halide (Scheme 1). The dye **OD3** was metathesized to the corresponding tetraphenylborate salt **OD4** by precipitation from acetonitrile/water NaBPh₄.



Scheme 1. Synthesis of D-*π*-A type pyridinium dyes **OD1–OD4** bearing various counter anions.

The solvatochromic spectral data of OD1-OD4 are summarized in Table 1 and the spectra of **OD3** in various solvents are shown in Fig. 1a (see Table S1 in Supporting Information for the molar extinction coefficients of OD1-OD4). Fig. 2a shows color changes of OD3 in various solvents. The color of OD3 in 1,4-dioxane, THF, acetone, and DMSO is yellow, but the color of OD3 in dichloromethane, dibromomethane, and diiodomethane is reddish-orange. The pyridinium dyes OD1-OD4 show absorption maxima at around 460-530 nm attributable to ICT excitation from diphenylamino group to pyridinium ring. The ICT absorption bands of the four dyes exhibit a general negative solvatochromism in non-halogenated solvents; with decreasing solvent polarity from DMSO ($\varepsilon_r =$ 47.24) to toluene ($\varepsilon_r = 2.38$), for example, the ICT absorption band of OD3 shifts from 438 nm to 459 nm. On the other hand, the dyes **OD1–OD4** showed the specific solvatochromism, leading to large bathochromic shift of ICT absorption band in halogenated solvents: although the $\varepsilon_{\rm r}$ value of dibromomethane ($\varepsilon_{\rm r} = 7.77$) is very close to that of THF ($\varepsilon_r = 7.52$), the ICT absorption band of **OD3** in dibromomethane occurs at 481 nm compared with 443 nm in THF. Moreover, as shown in Fig. 1b, the ICT absorption band in iodinated solvents such as iodobenzene and diiodomethane shows bathochromic shifts compared with those in chlorinated and brominated solvents. The large bathochromic shifts of ICT absorption band in iodinated

solvents were also observed in the cases of OD1-OD3 (Table 1). It is worthy to note here that the specific solvatochromism strongly depends on the counter anion of the dyes OD1-OD4, that is, the bathochromic shifts of ICT absorption band become larger in order of soft counter anion $Cl^- < Br^- < I^- < BPh_4^-$. In fact, as shown in Fig. 1c, the ICT absorption bands of the four dyes in dibromomethane show the large bathochromic shifts in order of OD1 < OD2 < OD3 < OD4. The color of OD1and OD2 in dibromomethane is orange, but the color of OD3 and OD4 in dichloromethane is reddish-orange (Fig. 2b). Fig. 3 clearly indicates that the wavenumbers (\tilde{v}) of absorption maxima for the ICT bands of the dyes OD1-OD4 depend on the type of halogen atom of halogenated solvents and the counter anion of the dyes. On the other hand, among polar solvents ($\varepsilon_r > 20$), the ICT absorption bands of **OD1–OD4** in ethanol appear at wavelengths longer than those of **OD1–OD4** in the aprotic solvents such as acetone, acetonitrile and DMSO (Table 1). It was suggested that the bathochromic shift of ICT absorption band in ethanol is contributable to stronger ICT characteristics, which are induced by the hydrogen bonding between hydroxyl group of ethanol and the counter anion of OD1-OD4.

Table 1. Solvatochromic spectral data of OD1-OD4

No.	Solvent	$\boldsymbol{\mathcal{E}}_{r}^{a}$	$\lambda_{\max}^{abs} [nm]^{b}$			
			OD1	OD2	OD3	OD4
1	1,4-dioxane	2.22	442	442	445	460
2	tetrachloromethane	2.24	_ ^c		488	464
3	toluene	2.38	_ ^c		459	470
4	bromoform	4.40	459	464	475	474
5	iodobenzene	4.59	475	480	485	486
6	chloroform	4.81	473	477	482	479
7	diiodomethane	5.32	480	494	497	497
8	bromobenzene	5.45	470	472	475	480
9	fluorobenzene	5.47	461	463	467	474
10	chlorobenzene	5.69	464	470	477	479
11	THF	7.52	438	440	443	458
12	dibromomethane	7.77	472	475	481	488
13	dichloromethane	8.93	468	473	480	487
14	acetone	21.10	443	443	443	443
15	ethanol	25.3	455	455	455	455
16	acetonitrile	36.64	441	440	440	440
17	DMSO	47.24	438	438	438	438
^a Dialactria constant (ref. 24) ^b The longest wavelength observation						

^a Dielectric constant (ref. 34). ^b The longest wavelength absorption maximum. ^c Poorly soluble



Fig. 1. Absorption spectra of a) OD3 in various solvents, b) OD3 in halogenated solvents, and c) OD1–OD4 in CH_2Br_2 .



Fig. 2. (a) Solvatochromic properties of **OD3** in various solvents. (b) Specific solvatochromic properties of **OD1–OD4** in CH₂Br₂.



Fig. 3. Plots of the experimental absorption maximum wavenumber (\tilde{v}) of **OD1–OD4** against the ε_r value of CH₂Cl₂, CH₂Br₂, and CH₂I₂.

To elucidate the influences of solvent polarity on the ICT bands of OD1-OD4, semi-empirical MO calculations of the dye cation were carried out by the INDO/S method35 using the SCRF Onsager Model after geometrical optimizations using the MOPAC/AM1 method.³⁶ The calculated absorption data are collected in Table 2. For all the solvents used, the calculations show that the first excitation bands of the dye cation are mainly assigned to a transition from HOMO to LUMO, where HOMO is mostly localized on the diphenylamino-carbazole moiety and LUMOs are mostly localized on the pyridinium moiety (Figs. 4a and b). The changes in the calculated electron density accompanying the first electron excitation are shown in Fig. 4c, which reveals that the ICT occurs from the diphenylamino-carbazole moiety to the pyridinium moiety. The calculation demonstrates that with decreasing solvent polarity from DMSO to 1,4-dioxane the ICT absorption bands show bathochromic shifts from 373 nm to 453 nm (Table 2). In order to see the influence of solvent polarity on the ICT absorption bands more explicitly, the wavenumbers (\tilde{v}) of the experimental absorption maxima for the ICT bands of OD3 and the calculated absorption maxima for the ICT bands of the dye cation are plotted against the ε_r value of solvent in Fig. 5a and Fig. 5b, respectively. The plot of the calculated absorption maximum against ε_r shows that the wavenumber increases dramatically with the increase in ε_r value from 1,4-dioxane $(\varepsilon_r = 2.22)$ to dichloromethane $(\varepsilon_r = 8.93)$, while in the range of ε_r value between dichloromethane ($\varepsilon_r = 8.93$) and DMSO ($\varepsilon_r = 47.24$) the wavenumber is increased gradually (Fig. 5b). On the other hand, the profile of plot of the experimental absorption maximum against ε_r differs considerably from that of the calculation: the ICT absorption bands of OD3 in halogeneted solvents are

located in the low-wavenumber range (Fig. 5a). In addition, as shown in Fig. 5c, the plot of the experimental absorption maximum against solvent polarity parameter $E_T(30)$ is the profile similar to the plot of Fig. 5a. However, when the plots of halogeneted solvents and alcohol solvents are excluded from the plot of Fig. 5a, the profile of the plot of Fig. 5a is similar to that of Fig. 5b. This result clearly shows that with increasing solvent polarity of nonhalogenated solvents, the ICT absorption band of **OD1–OD4** shows a hypsochromic shift, that is, the dyes **OD1–OD4** in non-halogenated solvents exhibit a general negative solvatochromism.



Fig. 4. (a) HOMO and (b) LUMO of the dye **OD** cation. The red and blue lobes denote the positive and negative phases of the coefficients of the molecular orbitals. The size of each lobe is proportional to the MO coefficient. (c) Calculated electron density changes accompanying the first electronic excitation of the dye cation. The black and white lobes signify decrease and increase in electron density accompanying the electronic transition, respectively. Their areas indicate the magnitude of the electron density change. (Light blue, green, blue, and red balls correspond to hydrogen, carbon, nitrogen, and oxygen atoms, respectively.)

 Table 2. Calculated absorption spectra for the dye OD cation

No.	Solvent	$\lambda_{\rm max}$ [nm]	CI component ^a
1	1,4-dioxane	453	HOMO→LUMO (72%)
2	tetrachloromethane	447	HOMO→LUMO (72%)
3	toluene	442	HOMO→LUMO (71%)
4	bromoform	405	HOMO→LUMO (70%)
5	iodobenzene	403	HOMO→LUMO (70%)
6	chloroform	404	HOMO→LUMO (70%)
7	diiodomethane	396	HOMO→LUMO (70%)
8	bromobenzene	398	HOMO→LUMO (70%)
9	fluorobenzene	400	HOMO→LUMO (70%)
10	chlorobenzene	397	HOMO→LUMO (70%)
11	THF	391	HOMO→LUMO (69%)
12	dibromomethane	389	HOMO→LUMO (69%)
13	dichloromethane	391	HOMO→LUMO (69%)
14	acetone	380	HOMO→LUMO (69%)
15	ethanol	379	HOMO→LUMO (69%)
16	acetonitrile	377	HOMO→LUMO (69%)
17	DMSO	373	HOMO→LUMO (69%)

^a The transition is shown by an arrow from one orbital to another, followed by its percentage CI (configuration interaction) component.



Fig. 5. Plots of (a) the experimental and (b) calculated absorption maximum wavenumber (\tilde{v}) of **OD3** against ε_r value of solvent. (c) Plots of the experimental absorption maximum wavenumber (\tilde{v}) of **OD3** against solvent polarity parameter $E_T(30)$. The numbers correspond to those of Tables 1 and 2, respectively. The circles in black, orange, blue, red, purple, and green show non-halogenated solvents, fluorobenzene, chlorinated solvents, brominated solvents, iodinated solvents, and ethanol, respectively.

In order to investigate the influence of solvent on the electronic ground-state structure of **OD1–OD4**, the ¹H NMR measurements in acetone-d₆ of a high ε_r value and THF-d₈ of a relatively low ε_r value as the non-halogenated solvents, and in CD₂Cl₂ as the halogenated solvent were performed. The ¹H NMR spectra of **OD3** in acetone-d₆,

withdrawing group such as rhodanine and dicyanomethylene units.³¹ Consequently, our results demonstrate that the halogen-halide anion interaction plays some non-negligible role here, but this interaction is surely not responsible for the specific solvatochromism in halogenated solvents, but only for the systematic shift within the series of dyes with various counter anions.



Fig. 6. ¹H NMR spectra of **OD3** in (a) acetone- d_6 , (b) THF- d_8 , and (c) CD₂Cl₂.



Fig. 7. ¹H NMR spectra of **OD1–OD4** in acetone-d₆.



Fig. 8. ¹H NMR spectra of **OD1–OD4** in CD₂Cl₂.

THF-d₈, and CD₂Cl₂ are shown in Fig. 6. Remarkable differences were observed between the halogenated and non-halogenated solvents: the chemical shifts of H_a, H_b, H_c, H_d, H_e, and H_f show upfield shifts on changing solvents from acetone- d_6 or THF- d_8 to CD_2Cl_2 . It is worth noting that these chemical shifts in CD₂Cl₂ show significantly upfield shifts compared to those in THF-d₈, although the ε_r value of CH₂Cl₂ is close to that of THF. Awwadi et al have demonstrated by theoretical and crystallographic studies for halogen-halide anion interaction between the halide anion and the halogen atom of halogenated solvents.³⁷ For the type of the halogen atom of halogenated solvents, the energy of halogen-halide anion interaction follows the order F < Cl < Br < I. Therefore, it is apparent that the observed upfield shifts of H_a, H_b, H_c, H_d, H_e, and H_f on changing solvents from acetone-d₆ or THF-d₈ to CD₂Cl₂ are attributed to a shift of the electronic structure of **OD1–OD4** depending on the order of halogen-halide anion interaction for the type of the halogen atom of halogenated solvents. In fact, the bathochromic shifts of ICT absorption band of OD1-OD4 in iodinated solvents such as iodobenzene and diiodomethane are larger than those in chlorinated and brominated solvents (Table 1 and Fig. 1b), which is good agreement with an increase in the energy of halogen-halide anion interaction for the type of the halogen atom of halogenated solvents. A more interesting result was obtained when a comparison is made for the ¹H NMR spectra of **OD1–OD4** in acetone-d₆ and CD₂Cl₂ (Figs. 7 and 8). There are little differences in these chemical shifts among the dyes **OD1–OD4** in acetone- d_6 , which adequately reflects the very similar ICT absorption bands of OD1-OD4 in acetone (Table 1). On the other hand, the chemical shift of H_a for the dyes **OD1–OD4** in CD₂Cl₂ depends on the type of counter anion of the dyes, that is, the chemical shift of H_a show the upfield shifts in order of soft counter anion $Cl^- < Br^- < I^- < BPh_4^-$. Moreover, the chemical shifts of H_b , H_c , and H_d for the dye **OD4** in CD₂Cl₂ show significantly upfield shifts compared to those for the dyes **OD1–OD3** in CD_2Cl_2 , which adequately reflects the ICT absorption bands of the dyes OD1-OD4 in dichloromethane: the ICT absorption bands of the four dyes in halogenated solvents show the large bathochromic shifts in order of **OD1** < **OD2** < **OD3** < **OD4** (Table 1). Awwadi et al have also showed that the energy of halogen-halide anion interaction for the type of the halide anion of counter anions follows the order $\overline{I} < Br^- < Cl^- < F^-$, which is in contrast to that for the type of halogen atoms of halogenated solvents. However, the bathochromic shifts of ICT absorption band of the four dyes in halogenated solvents become larger in order of soft counter anion of the dyes **OD1–OD4**; $CI^- < Br^- < I^- < BPh_4^-$ (Fig. 3), which is exactly opposite to an increase in the energy of halogenhalide anion interaction for the type of the halide anion of counter anions. Nevertheless, the ¹H NMR spectra of **OD1**-**OD4** in CD_2Cl_2 indicate that the halogenated solvents can significantly enhance the ICT characteristic of D- π -A type pyridinium dye with soft counter anion, leading to large bathochromic shift of ICT absorption band in halogenated solvents. On the other hand, the specific solvatochromism of dyes in halogenated solvents is also observed for neutral (non-ionic) D- π -A dyes having strong electron-

Conclusions

In order to gain greater insight into the influences of the electronic structures of D- π -A type pyridinium dye on the specific solvatochromism in halogenated solvents, we have designed and synthesized D- π -A type pyridinium dyes **OD1–OD4** bearing various counter anions $(X^- = Cl^-, Br^-, I^-, Br^-, I^-)$ or BPh_4^{-}). The dyes **OD1–OD4** showed the specific solvatochromism, leading to large bathochromic shift of ICT absorption band in halogenated solvents. It was found that the bathochromic shifts of ICT absorption band of OD1-OD4 in iodinated solvents are larger than those in chlorinated and brominated solvents, which is good agreement with an increase in the energy of halogen-halide anion interaction for the type of the halogen atom of halogenated solvents. The ¹H NMR study indicates that the halogenated solvents can significantly enhance the ICT characteristic of D- π -A type pyridinium dye with soft counter anion, leading to large bathochromic shift of ICT absorption band in halogenated solvents. Furthermore, this study revealed that the bathochromic shifts of ICT absorption band of the four dyes in halogenated solvents become larger in order of soft counter anion of the dyes **OD1–OD4**; $Cl^- < Br^- < I^- < BPh_4^-$, which is exactly opposite to an increase in the energy of halogen-halide anion interaction for the type of the halide anion of counter anions. Consequently, our results demonstrate that the halogen-halide anion interaction plays some non-negligible role here, but this interaction is surely not responsible for the specific solvatochromism in halogenated solvents, but only for the systematic shift within the series of dyes with various counter anions. Further studies on the specific solvatochromism of D- π -A type pyridinium dyes bearing various counter anions are now in progress to gain greater insight into the influences of number of halogen atoms of halogenated solvents on the specific solvatochromism.

Experimental section

4.1. General

TG-DTA was performed with a SII TG/DTA 6200. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer by ATR method. High-resolution mass spectral data were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. ¹H NMR and ¹³C NMR spectra were recorded on a Varian-500 (500 MHz) FT NMR spectrometer with tetramethylsilane as an internal standard. Absorption spectra of solution (2×10^{-5} M – 7×10^{-5} M) were observed with a Hitachi U-2910 spectrophotometer.

4.2. Synthesis of 1-butyl-4-(9-butyl-7-(diphenylamino)-9H-carbazol-2-yl)pyridinium chloride (OD1)

A solution of **1** (0.35 g, 0.75 mmol) and 1-chlorobutane (19.3 g) in dry toluene (50 ml) was stirred at 80 °C for 7 days. After concentrating under reduced pressure, the resulting residue was subjected to reprecipitation from CH₂Cl₂-hexane to give **OD1** (0.17 g, yield 41 %) as yellow solids; decomposition 256 °C. IR (ATR): $\tilde{v} = 1623 \text{ cm}^{-1}$. ¹H

NMR (500 MHz, acetone-d₆): $\delta = 0.84$ (t, J = 7.0 Hz, 3H), 1.01 (t, J = 7.5 Hz, 3H), 1.26–1.32 (m, 2H), 1.48–1.52 (m, 2H), 1.74–1.81 (m, 2H), 2.13–2.17 (m, 2H), 4.42 (t, J = 7.0 Hz, 2H), 4.85 (t, J = 7.0 Hz, 2H), 6.98 (dd, J = 1.5 and 8.0 Hz, 1H), 7.08–7.12 (m, 2H), 7.14–7.18 (m, 4H), 7.24 (d, J = 1.5 Hz, 1H), 7.32–7.37 (m, 4H), 7.91 (dd, J = 1.5 and 8.5 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 8.31 (d, J = 8.5 Hz, 1H), 8.38 (d, J = 1.5 Hz, 1H), 8.72 (d, J = 7.0 Hz, 2H) 9.22 (d, J = 7.0 Hz, 2H) ppm. ¹³C NMR (500 MHz, CDCl₃): $\delta = 13.5$, 13.8, 19.4, 20.4, 31.1, 33.6, 42.8, 60.6, 103.6, 108.0, 116.8, 117.1, 118.4, 120.7, 121.8, 123.3, 124.4, 124.6, 126.8, 128.9, 129.3, 141.2, 143.3, 144.4, 147.8, 148.4, 157.1 ppm. HRMS (ESI): calcd. for [M–Cl]⁺ 524.30602; found 524.30609.

4.3. Synthesis of 1-butyl-4-(9-butyl-7-(diphenylamino)-9H-carbazol-2-yl)pyridinium bromide (OD2)

A solution of 1 (0.35 g, 0.75 mmol) and 1-bromobutane (8.2 g) in dry acetonitrile (90 ml) was stirred at 80 °C for 4 days. After concentrating under reduced pressure, the resulting residue was subjected to reprecipitation from CH₂Cl₂-hexane to give **OD2** (0.40 g, yield \$9 %) as dark brown solids; decomposition 263 °C. IR (ATR): $\tilde{v} = 1623$ cm⁻¹. ¹H NMR (500 MHz, acetone-d₆): $\delta = 0.84$ (t, J = 7.5Hz, 3H), 1.01 (t, J = 7.5 Hz, 3H), 1.26–1.34 (m, 2H), 1.46– 1.53 (m, 2H), 1.76-1.81 (m, 2H), 2.13-2.17 (m, 2H), 4.44 (t, J = 7.0 Hz, 2H), 4.87 (t, J = 7.5 Hz, 2H), 6.98 (dd, J =1.5 and 8.0 Hz, 1H), 7.08-7.12 (m, 2H), 7.15-7.18 (m, 4H), 7.24 (d, J = 1.5 Hz, 1H), 7.33–7.37 (m, 4H), 7.92 (dd, J =1.5 and 8.0 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.42 (d, J = 1,5 Hz, 1H), 8.74 (d, J = 7.0 Hz, 2H), 9.26 (d, J = 7.0 Hz, 2H) ppm. ¹³C NMR (500 MHz, $CDCl_3$): $\delta = 13.5, 13.9, 19.4, 20.4, 31.1, 33.6, 42.9, 60.6,$ 103.6, 108.0, 116.8, 117.1, 118.4, 120.7, 121.8, 123.3, 124.4, 124.6, 126.8, 128.8, 129.3, 141.1, 143.3, 144.3, 147.7, 148.4, 157.1 ppm. HRMS (ESI): calcd. for [M-Br]⁺ 524.30602; found 524.30621.

4.4. Synthesis of 1-butyl-4-(9-butyl-7-(diphenylamino)-9H-carbazol-2-yl)pyridinium iodide (OD3)

A solution of 1 (0.3 g, 0.64 mmol) and 1-iodobutane (7.1 g) in dry acetonitrile (90 ml) was stirred at 80 °C for 70 h. After concentrating under reduced pressure, the resulting residue was subjected to reprecipitation from CH2Cl2hexane to give **OD3** (0.33 g, yield 79 %) as orange solids; decomposition 276 °C. IR (ATR): $\tilde{v} = 1620 \text{ cm}^{-1}$. ¹H NMR (500 MHz, acetone-d₆): $\delta = 0.84$ (t, J = 7.5 Hz, 3H), 1.01 (t, J = 7.5 Hz, 3H), 1.28–1.32 (m, 2H), 1.48–1.53 (m, 2H), 1.76-1.82 (m, 2H), 2.12-2.17 (m, 2H), 4.37 (t, J = 7.0 Hz, 2H), 4.86 (t, J = 7.5 Hz, 2H), 6.98 (dd, J = 1.5 and 8.0 Hz, 1H), 7.06–7.12 (m, 2H), 7.14–7.18 (m, 4H), 7.24 (d, J = 1.5 Hz, 1H), 7.32–7.37 (m, 4H), 7.92 (dd, J = 1.5 and 8.5 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.5 Hz, 1H), 8.41 (d, J = 1.5 Hz, 1H), 8.74 (d, J = 7.0 Hz, 2H), 9.22 (d, J =7.0 Hz, 2H) ppm. ¹³C NMR (500 MHz, acetone-d₆): δ = 13.8, 14.2, 20.1, 21.0, 31.9, 34.1, 43.2, 61.3, 105.0, 109.8, 117.8, 118.1, 119.7, 121.6, 122.9, 124.2, 125.3, 125.4, 127.3, 130.3, 130.5, 142.2, 144.2, 145.2, 148.9, 149.1,

157.9 ppm. HRMS (ESI): calcd. for $[M-I]^+$ 524.30602; found 524.30609.

4.5. Synthesis of 1-butyl-4-(9-butyl-7-(diphenylamino)-9H-carbazol-2-yl)pyridinium tetraphenylborate (OD4)

OD3 metathesized was to the corresponding tetraphenylborate salt OD4 as dark brown solids by precipitation from acetonitrile/water NaBPh₄; decomposition 187 °C. IR (ATR): $\tilde{v} = 1621, 732, 702 \text{ cm}^{-1}$. ¹H NMR (500 MHz, acetone-d₆): $\delta = 0.84$ (t, J = 7.5 Hz, 3H), 1.00 (t, J = 7.5 Hz, 3H), 1.25–1.31 (m, 2H), 1.45–1.50 (m, 2H), 1.76–1.82 (m, 2H), 2.12–2.17 (m, 2H), 4.41 (t, J = 7.0 Hz, 2H), 4.77 (t, J = 7.5 Hz, 2H), 6.75–6.79 (m, 3H), 6.92–6.97 (m, 6H), 6.98 (dd, J = 2.0 and 8.5 Hz, 1H), 7.09– 7.12 (m, 2H), 7.14–7.17 (m, 4H), 7.24 (d, J = 2.0 Hz, 1H), 7.33–7.36 (m, 10H), 7.89 (dd, J = 2.0 and 8.5 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 8.30-8.32 (m, J = 8.5 Hz, 2H), 8.65 (d,J = 7.0 Hz, 2H), 9.06 (d, J = 7.0 Hz, 2H) ppm. ¹³C NMR (500 MHz, acetone-d₆): $\delta = 13.8$, 14.1, 20.1, 21.0, 31.9, 34.0, 43.2, 61.4, 105.0, 109.6, 117.8, 118.1, 119.8, 121.7, 122.3, 122.9, 124.2, 125.3, 125.5, 126.00, 126.02, 126.05, 126.07, 127.3, 130.3, 130.5, 137.01, 137.03, 137.04, 137.05, 142.2, 144.2, 145.1, 148.9, 149.1, 157.9, 164.4, 164.8, 165.2, 165.6 ppm. HRMS (ESI): calcd. for $[M-BPh_4]^+$ 524.30602; found 524.30591.

4.6. Computational methods

The semi-empirical calculations were carried out with the WinMOPAC Ver. 3.9 package (Fujitsu, Chiba, Japan). Geometry calculation of compound 2 in the ground state was made using the AM1 method.³⁶ The geometry was completely optimized (keyword PRECISE) by the eigenvector following routine (keyword EF). Experimental absorption spectra of the compound was compared with their absorption data by the semi-empirical method INDO/S (intermediate neglect differential of overlap/spectroscopic)³⁵ using the SCRF Onsager Model. All INDO/S calculations were performed using single excitation full SCF/CI (self-consistent field/configuration interaction), which includes the configuration with one electron excited from any occupied orbital to any unoccupied orbital, where 100 configurations were considered [keyword CI (15 15)].

Keywords: Pyridinium dye; Solvatochromism; Donor-piacceptor system; Halogenated solvent; Halogen-halide anion interaction

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