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10.1039/x0xx00 for an anion: Unique fluorescence behaviour depending on
000x the binding anion's electrophilic property

Hironori Izawa,^{*a} Shoji Nishino,^a Masato Sumita,^{*b} Masaaki Akamatsu,^c Kenji
Morihashi,^d Shinsuke Ifuku,^a Minoru Morimoto,^a and Hiroyuki Saimoto^a

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We have designed a novel 1,8-naphthalimide derivative with an open space for an anion. Computational calculation had predicted that the space could trap various anion species and photo-induced charge transfer depending on the anion's electrophilic property. Indeed, the fluorescence behaviour of the 1,8-naphthalimide derivative complexes with each anion is consistent with the computational prediction.

Anion recognition chemistry using small molecules has become an area of significant importance because anions play crucial roles in the area of biology, medicine, and catalysis, in addition to the demand to detect pollutant anions.¹ Although many sophisticated anion sensors containing a receptor moiety such as amide/urea², amine/ammonium³, pyrrole⁴, or indole⁵ have been prepared,⁶ the interest and the requirement still have not been lost.⁷

1,8-Naphthalimide derivatives have received much attention because they are applicable as sensor materials⁸ and fluorescent markers for medical and biological purposes⁹ by virtue of their characteristic photo-induced properties. The considerable interest in these derivatives as photoactive components is associated with the electron-withdrawing nature of the naphthalimide ring in their excited state, which results in interesting phenomena: a charge-transfer reaction with an anion^{8b} and the formation of excimers¹⁰ or exciplexes¹¹. We believe that rational design gives the 1,8-naphthalimide derivatives a selective/dominant phenomenon.

In this study, we have designed 1-methyl-3-(*N*-(1,8-naphthalimidyl)ethyl)imidazolium (MNEI), composed of the 1,8-naphthalimide group and an imidazole group, and an ethyl linker (Fig. 1A).[†] Previously reported anion sensors characterized by 1,8-naphthalimide have a receptor moiety that discriminates a specific anion.^{8b} However, we have used a cationic imidazolium group as an unspecific receptor for an anion. Figure 1B shows the calculated structure of MNEI *in vacuo* at the density functional theory (DFT) level (see the Supplementary Information about the computational details). The open space between the 1,8-naphthalimide group and the imidazolium group can trap the anion because of both electrostatic interaction with the imidazolium and an anion- π interaction¹² with the 1,8-naphthalimide, which might perturb MNEI.

DFT calculation indicates the existence of several charge-transfer (CT) states from an anion to MNEI (naphthalimide group) appearing between the ground state and the HOMO/LUMO excited state of MNEI (S_{M1}) in spite of their low oscillator strength. We can predict that these CT states are largely influenced by the electrophilic property of anion atoms (electronegativity) in contrast to the S_{M1} state of MNEI. Indeed, Fig. 2 shows the correlation between the electronegativity of an anion (halogen series: X) and the anion to the MNEI LUMO CT (CT_0) state. That is, as electronegativity decreases, the relative energy of the CT_0 states stabilizes. Moreover, the anion to MNEI LUMO+1 CT (CT_1) states also stabilize enough to degenerate with the S_{M1} states as electronegativity decreases. The similar tendency is also obtained at the CAM-B3LYP¹³ level (see the Supplementary Information). This means that the CT states substantially influence the photo-induced process of the MNEI complex with an anion that has low electronegativity.

We expect that the difference in the CT states depending on the electronegativity of the anion is reflected in the photophysics (fluorescence or its quenching) of the MNEI complexes because the irradiative transition from the S_{M1} to CT_1 state easily occurs when the S_{M1} state degenerates with the CT_1 state, as shown in Fig. 3. Because the electrostatic interaction between the neutralized anion and MNEI after the transit to the CT state disappears, the emission

of the neutralized anion is a possible relaxation process. This is supported by the fact that the CT states of MNEI-Br/I are more stable than their S_0 states in their dissociation limit. Hence, we guess that the photo-induced process of MNEI complexes with low-electronegative anions is nonradiative. Based on the above considerations, we have investigated the photophysical properties of the potentially versatile anion sensor of MNEI with various anions.

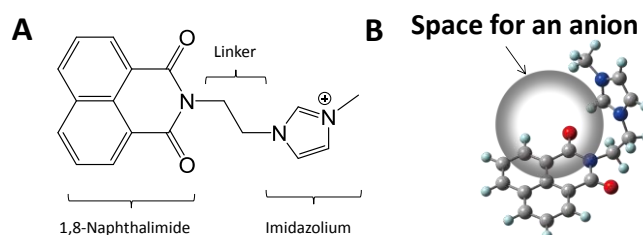


Fig. 1. Chemical structure of MNEI (A) and calculated structure of MNEI *in vacuo* (B) at the B3LYP/6-31G* level.

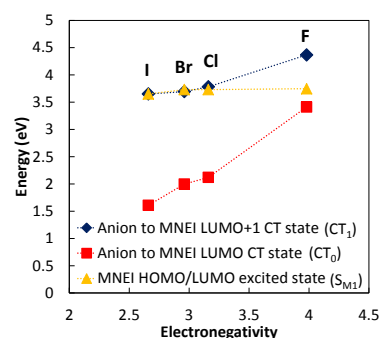


Fig. 2. Calculated correlations between the electronegativity of an anion (halogen series) and the vertically excited energies of S_{M1} , CT_0 , and CT_1 states (relative to each ground state of MNEI-X, X = F, Cl, Br, I) at the B3LYP/6-31G* level.

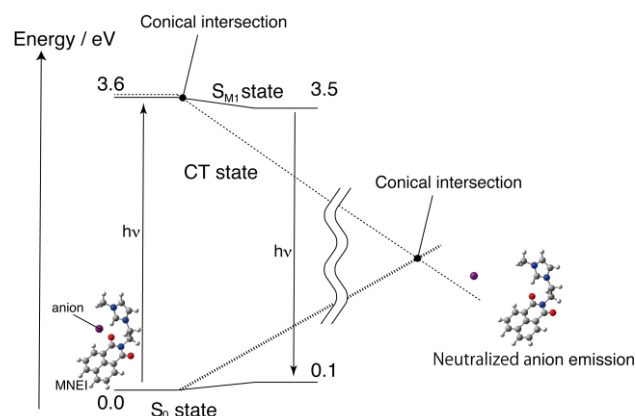


Fig. 3. Schematic energy diagram. Values estimated by the isolated MNEI relaxation process in the S_{M1} state are given in eV at the B3LYP/6-31G* level. Bold lines are the S_{M1} and S_0 states of MNEI. CT state is shown by the broken line, and the corresponding ground state is shown by the hashed line. In the case of MNEI-Br/I, the S_{M1} state almost degenerates with CT state at vertically excited points. In the relaxation process in the S_{M1} state, MNEI-Br/I easily transits to the CT states. MNEI-Br/I in the CT state is stabilized with neutralized Br/I atom emission.

MNEI was synthesized as Cl salt (MNEI-Cl) from 1,8-naphthalic anhydride in two steps. The structure of the MNEI-Cl was confirmed by nuclear magnetic resonance (NMR), infrared (IR), mass spectroscopies, and elemental analysis. Details are described in the Supplementary Information.

Figure 4A shows UV-Vis spectra of 0.07-1.45 mM MNEI-Cl aqueous solutions. In the spectra, absorption peaks at around 345 nm are shown, which is consistent with the absorption peak due to the 1,8-naphthalimide group in water¹⁴ and the calculated vertically excited energy to the S_{M1} state of the MNEI *in vacuo* (341 nm). Figure 4B shows fluorescence emission spectra excited at 380 nm of 0.07-4.00 mM MNEI-Cl aqueous solutions. In the fluorescence emission spectra, two significant peaks appear. One is the narrow emission peak at around 400 nm due to the 1,8-naphthalimide group¹⁴. Computationally, this emission is attributed to the radiative transition from the minimum in the S_{M1} state of the MNEI, which is reached by bond alternation of the 1,8-naphthalimide group, though computational fluorescence is overestimated as 360 nm. The other is the broad peak at around 480 nm due to an excimer of the 1,8-naphthalimide groups caused by aggregation^{10, 15}. General 1,8-naphthalimide-based anion sensors were modified to visualize absorbance and/or fluorescence.^{8b} Nevertheless, the excimer formation enables the visualization of the fluorescence emission of MNEI. The fluorescence emission peak due to the excimer gradually grows as the concentration increases from 0.07 mM to 2.90 mM. Above 2.90 mM, both fluorescence emissions are quenched, which is probably due to concentration quenching.¹⁶ Note that excitation spectra (Fig. S1) also suggested the aggregation of MNEI, in which the excitation spectra changed distinctly at concentrations higher than 0.29 mM.

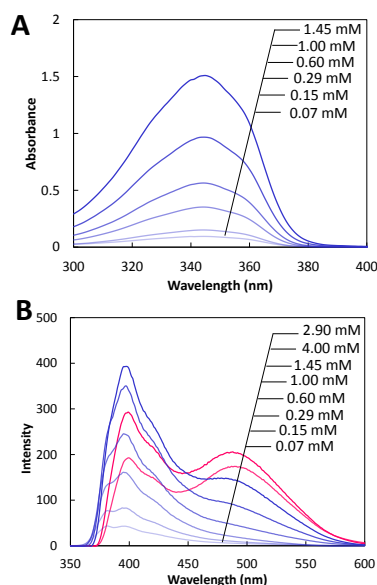


Fig. 4. UV-Vis (A) and fluorescence spectra (B) of MNEI-Cl in water.

In order to confirm the effect of a salt on the photophysics, absolute quantum yield (Φ) of MNEI-Cl in the presence or absence of NaCl was investigated. The quantum yield of the 1.45 mM MNEI-Cl in 210 mM NaCl solution ($\Phi = 0.144$) was slightly lower than that in water ($\Phi = 0.173$). Indeed, the fluorescence intensities gradually decreased as NaCl increases (Fig. 5A). To reveal the reason for the lower fluorescence in the presence of NaCl, Stern-volmer relation¹⁷ between MNEI-Cl and NaCl was investigated (Fig. 5C), in which linear relations were shown. This result suggests the quench by adding NaCl is caused by increased quantity of the MNEI-Cl complex in the solution and the complex is 1:1 stoichiometry. Besides, non-specific interaction between MNEI and Na^+ and/or Cl^- was not serious in the system.

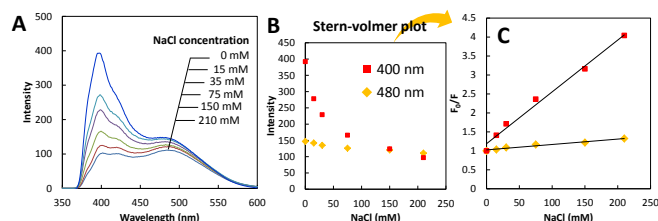


Fig. 5. Fluorescence spectra of the 1.45 mM MNEI-Cl in the presence of NaCl (A). Fluorescence intensities at 400 nm and 480 nm (B) were applied to the Stern-volmer plots (C).

UV-Vis and fluorescence spectra of MNEI-Cl in the presence of a sufficient amount of salt have been investigated to evaluate the effect of the anion species on the photophysics. Figure 6A shows UV-Vis spectra of 1.45 mM MNEI in 210 mM sodium salt (NaF, NaCl, NaBr, NaI, CH_3COONa , $NaSCN$, $NaN(CN)_2$, or NaOH) aqueous solutions. In most cases except for NaOH, the spectra are similar to the spectrum of MNEI-Cl in water, as shown in Fig. 6A. In order to investigate the cause of the blue shift observed only on NaOH, the 1H NMR spectrum of the 1.5 mM MNEI in 210 mM NaOD- D_2O solution was measured, where signals attributed to a hydrolyzed 1,8-naphthalimide group were shown (Fig. S2). This observation revealed that the distinct change was caused by a hydrolysis in alkaline condition. Indeed, there is a report concerning hydrolysis of 1,8-naphthalimide derivatives in alkaline aqueous solution.¹⁸ Figure 6B shows the fluorescence emission spectra of the above solutions. Although there is no discrepancy in the UV-Vis spectra except for NaOH, the fluorescence intensities are clearly varied in the salt species. To confirm the expected relationship between intensity and the electrophilic property, the fluorescence intensities at 400 nm and 480 nm were plotted as a function of electron negativity¹⁹ of the charged atom (Fig. 7A). Interestingly, the fluorescence intensities clearly decrease as the electronegativity decreases. This tendency corresponds to the computational result of the correlation between electronegativity and CT states as shown in Fig. 2. Although we further considered the solution pH and atomic radius (Fig. S3), a better correlation was not shown. Note that the maximum excitation wavelength of MNEI does not depend on the presence of a salt.

Furthermore, we have investigated fluorescence emission spectra of the 1.45 mM MNEI in 210 mM $NaHCO_3$ or NaH_2PO_4 aqueous solution, where the spectra were almost same as that in 210 mM CH_3COONa solution. This result indicates the MNEI shows the fluorescence behaviour depending on electronegativity even in the case of multivalent anions.

As mentioned above, the presence of the aggregate of MNEI in 1.45 mM solution was suggested, and this might relate to the fluorescence behaviour of MNEI. Hence, the UV-Vis (Fig. 6C) and the fluorescence emission spectra excited at 345 nm (Fig. 6D) of the 0.07 mM MNEI-Cl solution were further investigated because it was supposed that the MNEI molecules would not form an aggregation at 0.07 mM, as described in the Supplementary Information. Although there was no difference in the UV-Vis spectra, the fluorescence intensity changed in accordance with the anion's electronegativity (Fig. 7B). These results are consistent with those at 1.45 mM, indicating that the difference in fluorescence intensity caused by the binding anion occurs without the aggregation. Besides, 1H NMR analyses of 1.45 mM MNEI in 210 mM NaF/ D_2O (showing strong fluorescence) and NaI/ D_2O (showing extremely weak fluorescence) were performed to confirm the structural difference between MNEI-F and MNEI-I. However, there is no difference in the spectra (Fig. S4). These results indicate that the difference in fluorescence intensity is caused by the expected CT. As shown in Fig. 2, the CT_1 states of MNEI-I/Br almost degenerate with the S_{M1} states of MNEI. Hence, after MNEI-Br/I is excited to the S_{M1} state, it is easily expected to undergo the internal transition to the CT_1 state *via* a conical intersection, as shown in Fig. 3.²⁰ Once CT occurs, all CT states are stabilized by the emission of neutral Br/I radicals. It is

noteworthy that there is a possible route to the CT state during excimer formation because the quenching behaviour in the 1.45 mM solutions is more effective than that in the 0.07 mM solutions. We speculate that this CT results in the quenching process, which we will elucidate in our future work.

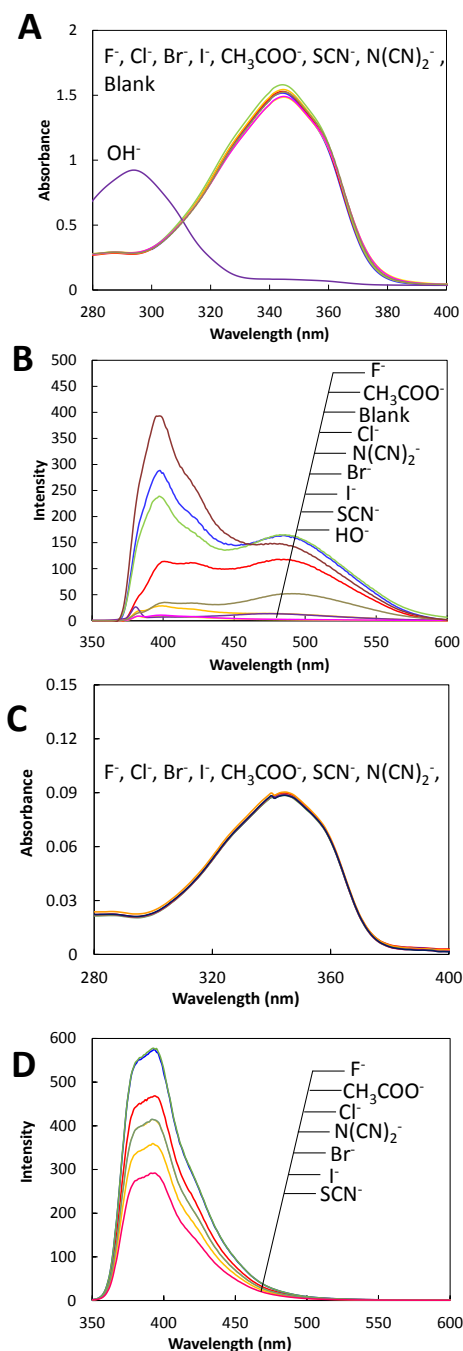


Fig. 6. UV-Vis and fluorescence emission spectra of 1.45 mM (A, B) or 0.07 mM MNEI-Cl (C, D) in 210 mM Na salt solutions.

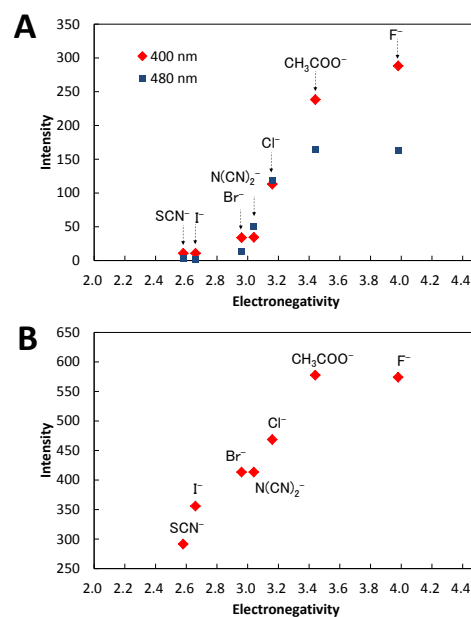


Fig. 7. Correlations between fluorescence intensity of 1.45 mM (A) or 0.07 mM (B) MNEI solution and electron negativity of the charged atom.

Conclusions

We have synthesized a novel 1,8-naphthalimide derivative [1-methyl-3-(*N*-(1,8-naphthalimidyl)ethyl)imidazolium, MNEI] through computational design. Because of the presence of an open space, MNEI plays a functional role as a host of anions. DFT calculations suggest the photophysics (fluorescence or its quenching) of the MNEI complexes with anions are affected by their CT states where the charge of the anion transfers to MNEI. Indeed, the fluorescence intensity is changed in accordance with the anion's electrophilic property, in which the fluorescence intensity clearly decreases as the electronegativity decreases. The proposed concept using CT would provide new directions to develop new 1,8-naphthalimide-based functional molecules and materials.

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Notes and references

^a Graduate School of Engineering, Tottori University, 4-101 Koyama-Minami, Tottori 680-8550, Japan.

^b National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

^c Department of Pure and Applied Chemistry, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan.

^d Department of Chemistry, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571, Japan.

† Though the 1,8-naphthalimide derivative with a longer alkyl linker and an imidazolium group has been prepared for an organic light-emitting diode,²¹ the application of the naphthalimide derivatives as versatile anion sensors has not been exploited.

Electronic Supplementary Information (ESI) available: Materials and methods, Computation details, and other supplementary data. See DOI: 10.1039/c000000x/

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