Intramolecular Fluorescence Quenching in Ferrocene-Naphthalimide Dyads

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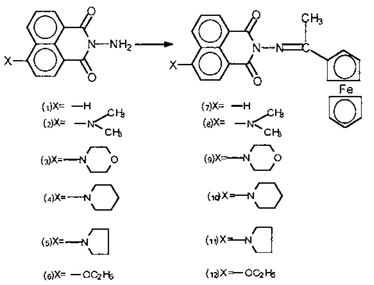
The intramolecular fluorescence quenching in ferrocenoyl naphthalimide dyads has been studied. In the dyads, the singlet excited state of naphthalimide (NA) could be effectively quenched by the ferrocene center. When ferrocene (Fc) was oxidized chemically, the intramolecular electron transfer from the oxidized ferrocene (Fc^+) would be inhibited and the fluorescence of NA moiety would be recovered.

Donor-acceptor compounds are of both scientific and industrial interest not only as models for the investigation of electron transfer, but also as basic materials for advanced technology, such as photo-optical devices. Typically photoactive donor-bridge-acceptor dyads are based on composites containing chromophoric donor moieties and suitable electron acceptors. Ferrocene (Fc) is one of the most common organometallic subunits and a good electron donor and it can be reversibly oxidized. There have been several reports of ferrocene-substituted multicomponent molecules in the literature.[1-3] For some porphyrin-ferrocene assembly, intramolecular quenching of porphyrin chromophore fluorescence by Fc was observed. Recently, a series of covalent linked fullerene-ferrocene dyads were reported as the evidence that the ferrocenyl center reduces the fullerene excited singlet states via intramolecular electron transfer.[4] The lowest excited singlet state of Fc is higher than that of C_{60}, ruling out any undesired singlet energy transfer from the excited fullerene to the Fc moiety. In recent years, fluorophores based on naphthalene nucleus have aroused our interests because of their potential use in fluorescent probes[5] and antenna moiety in laser dyes.[6] Here we report fluorescent properties of ferrocenoyl 1,8-naphthalimide dyads (NA-Fc). Naphthalimide (NA) has higher fluorescence quantum yield and its emission band could be red-shifted by 4-position substitution.[7] Because that Fc has oxidation potential +0.50 V (SCE), there is an electron transfer from Fc to NA and the fluorescence of NA would obviously quenched by this intramolecular electron transfer. When Fc is oxidized electrochemically or chemically, the intramolecular electron transfer from the oxidized ferrocene (Fc^+) would be inhibited and the fluorescence of NA moiety should be recovered. At this time one expect that the intramolecular energy transfer from NA to Fc^+ would be inhibited and the fluorescence of NA could be recovered completely. This kind of dyads would be more significance for the application. The chemical structures of the dyads in this study are shown in scheme 1. The preparation of dyads will be published in elsewhere in detail.[8] The absorption spectra data of dyads NA-Fc are summarized in Table1. As expected due to the low absorption of the Fc chromophore (λ_{max}^{ab} = 440 nm, ε = 90 M^{-1} cm^{-1}) compared to the NA nucleus, absorption spectra of dyads NA-Fc are nearly identical to that of the corresponding NA and to that of the mixtures of NA+Fc (1:1 molar ratio). No additional bands due to the charge transfer are observed. This indicates there is relative weak or little ground state electronic interaction between two moieties. It should be noted that compared with NA about 2—5 nm blue shift in the absorption spectra were observed for the dyads.



Scheme 1.

Table 1. Absorption spectra data (λ_{max}^{ab} /nm and ε /$M^{-1}cm^{-1}$) of compounds 1-12 in CH_3CN (1×10^{-4} M)

Compound	1	2	3	4	5	6
λ_{max}^{ab}/nm	337	425	401	415	451	370
$\varepsilon \times 10^{-4}$	1.19	1.25	1.30	1.27	1.26	1.25
Compound	7	8	9	10	11	12
λ_{max}^{ab}/nm	333	422	395	411	449	367
$\varepsilon \times 10^{-4}$	0.95	0.93	1.04	1.08	0.93	1.20

Emission spectra data of the compounds and cyclic voltammogram data $E_{Ox}^{1/2}$ (vs SCE) of dyads are summarized in Table 2. The fluorescence spectra of dyads are in agreement with their mirror image of UV-Vis absorption spectra. It is remarkable that compared to NA, the large decrease of fluorescence intensity in dyads was observed. The decrease is attributed to the intramolecular singlet states quenching of the NA by the Fc centers. The lowest singlet excited state of Fc is 2.46 eV[9] and generally lower than (in some case nearly equal to) that of NA derivatives, which do not rule out the singlet energy transfer from NA to Fc. This process would quench (may be obviously) the fluorescence of NA. Meanwhile, because that Fc has oxidation potential +0.50 V (SCE),[9] there is an electron transfer from Fc to NA and the fluorescence of NA would also obviously quenched by this intramolecular electron transfer. The free energy ΔG_{CS} for charge separation from the excited NA moiety to Fc can be calculated using eqn.:[10, 5] $\Delta G_{CS} = E_{Ox} - E_{Red} - E_s - (e_0^2/\varepsilon_s r_{12})$, where E_{Ox} is the oxidation potential energy of the donor, E_{Red} is the reduction potential energy of the acceptor, E_s is the potential energy of first excited singlet state of the donor, e_0 is the charge of an electron, ε_s is the static dielectric constant of solvent, and r_{12} is the center-to-center distance between the donor and acceptor. E_{Red} of 4-pyrrolidine-NA is -1.71 eV *vs* SCE[9, 10]. When E_s of 4-pyrrolidine-NA is taken as ~2.4 eV in CH_3CN.[5, 7, 9,

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[10] The ΔG_{CS} for dyad 11 is calculated to be ca. –0.77 eV (17.7 kcal/mol). The enough negative value of ΔG_{CS} shows that for dyad 11 the intramolecular electron transfer between Fc and NA is thermodynamically feasible. It can be expected that the fluorescence of NA in the dyads would be obviously quenched by Fc via intramolecular electron transfer from Fc to NA.

Table 2. Emission spectra data (1.0×10^{-4} M in CH_3CN, excited at the maximum absorption wavelengths, room temperature. The emission intensity data were obtained divisionally by the absorbance at excited wavelength) and cyclic voltammogram data $E_{Ox}^{1/2}$ (vs SCE) of compounds (1.0×10^{-4} M in CH_3CN using 0.1 M $[n\text{-}Bu_4N]\text{-}ClO_4$ as electrolyte)

Compound	2	3	4	5	6
λ^{fl}_{max}/nm	527.4	528.2	539.2	526.1	435.3
Intensity	0.314	0.626	0.434	1.280	0.377
Compound	8	9	10	11	12
λ^{fl}_{max}/nm	537.0	542.0	535.0	521.1	410.3
Intensity	0.054	0.086	0.060	0.086	0.113
$E_{Ox}^{1/2}$ / V	0.22	0.30	0.27	0.23	0.27

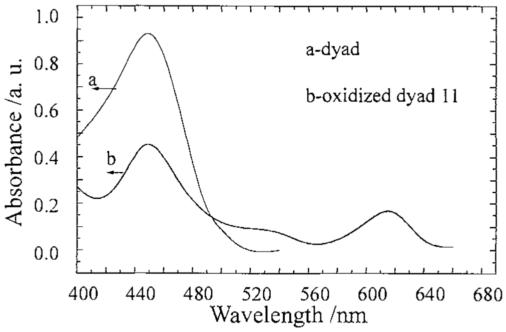

Figure 1. Absorption spectra of neutral and oxidized dyad 11.

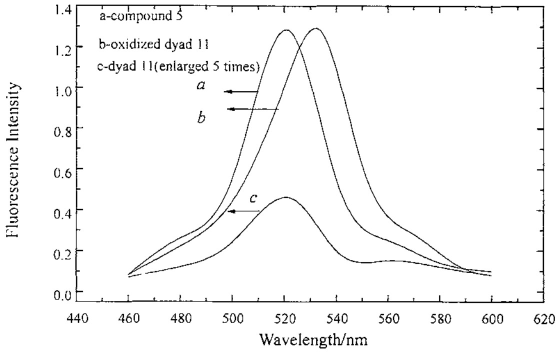

Figure 2. Emission spectra of compound 5, neutral dyad 11 and oxidized dyad 11.

The oxidation of dyad 11 was performed with ferricinium tungstosilicate in CH_3CN under Argon,[11] its absorption spectra and emission spectra were recorded *in situ* and showed in Figure 1 and 2. Comparing to the absorption spectra of neutral state of dyad 11, a new band with peak wavelength of 618 nm attributed to the absorption of ferricinium could be clearly found for oxidized dyad 11. From the emission spectra, a recovered fluorescence emission of NA was observed for oxidized dyad 11. When Fc is oxidized chemically, the intramolecular electron transfer from the oxidized ferrocene (Fc^+) would be inhibited and the fluorescence of NA moiety is recovered completely shown in Fig. 2. The cyclic voltammogram of dyad 11 shows one oxidation wave corresponding to $E_{Ox}^{1/2}$ (Fc^+-NA /Fc-NA) = +0.23 V(vs SCE). The effective singlet energy transfer from the excited NA moiety to the Fc^+ in oxidized dyad 11 may be ruled out due to the very low absorption of Fc and the very small spectral overlap between the emission of NA and the absorption of Fc^+-NA. For another dyads the fractions of fluorescence quenching of NA moieties by intramolecular electron transfer and energy transfer are being quantitatively measured.

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