# Syntheses of New Sensitizer–Donor Dyad Compounds with a Rigid Spacer

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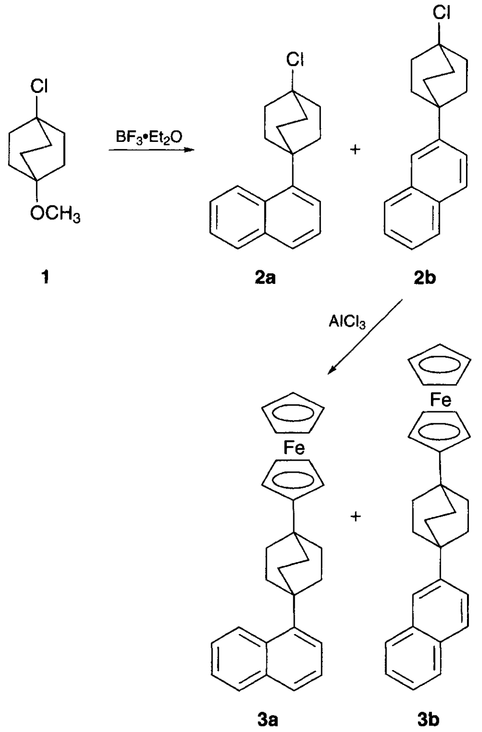
New sensitizer–donor dyads with a rigid spacer are synthesized from bicyclo[2.2.2]octane possessing both ether and halide active groups, which react selectively and successively with two kinds of aromatic molecules by making use of two types of Friedel–Crafts alkylation catalysts.

Photoinduced electron transfer plays an important role in photosynthetic solar energy conversion.[1–8] In our laboratory, artificial molecular devices for solar energy conversion that mimic the photosynthetic reaction centre were developed by the use of the Langmuir–Blodgett (LB) technique.[9,10] In such molecular devices, the arrangement of the various functional moieties was controlled spatially across the films at the molecular level. In a series of folded type sensitizer (S) and electron-donor (D) dyads in previous work, however, the dyad molecules in the LB films took many conformations due to the flexibility of the longer alkyl chain of the dyads, so that a clear dependence of the photoinduced electron transfer rate on the alkyl chain length, *i.e.* S–D distance, was not observed.[10] For this reason, we are studying the chain length dependence by using a series of linear-type S–D dyads, in which the S and D moieties are linked by a single alkyl chain. In closely packed LB films, the alkyl chain is considered to be extended and the distance between S and D to be controlled merely by changing the alkyl chain length.[11] In order to confirm the reasonable rates of electron transfer in such ideal S–D systems, it is interesting to have a standard S–D dyad in which these chromophores are separated at a fixed distance. In addition, precise comparison of the photoinduced electron transfer quenching rates between S–D dyads linked with either an extended four-carbon alkyl chain spacer or a rigid bicylo[2.2.2]octane unit with almost the same spacer length may provide us with knowledge of the effect of the number of paths in the 'through-bond' mechanism of electron transfer.

In this work, bicyclo[2.2.2]octane was used as a spacer between two chromophores[4,6] that satisfy the requirements mentioned above. The resulting rigid dyad molecule contains a naphthalene and a ferrocene moiety, as S and D, respectively. Friedel–Crafts alkylation was used for attaching these functional moieties directly to the bicyclooctane spacer. Selective alkylation was achieved by varying the alkylation catalyst, as boron trifluoride is known to act more effectively towards ethers and alcohols than towards halides.[12] As would be expected, bicyclo[2.2.2]octane possessing both ether and halide groups reacted selectively with naphthalene and ferrocene at different bridgehead positions by making use of the appropriate catalysts. This method will be widely applicable in the preparation of rigid compounds containing two kinds of aromatic moieties as their functional groups.

The new rigid S–D dyads **3a** and **3b** were synthesized by the reaction sequence shown in Scheme 1. 1-Chloro-4-methoxybicyclo[2.2.2]octane **1** was synthesized from 4-methoxybicyclo[2.2.2]octane-1-carboxylic acid[13] by adopting the procedure of Becker *et al.*[14] Using a boron trifluoride–diethyl ether complex as a Lewis acid catalyst, Friedel–Crafts alkylation of naphthalene with **1** afforded regioisomeric naphthyl compounds **2a** and **2b**. The rigid S–D dyads **3a** and **3b** were obtained from **2a** and **2b** by Friedel–Crafts alkylation of ferrocene using aluminium chloride as a catalyst. For the reference compounds of the rigid S–D dyads, a methyl group was substituted for the ferrocenyl donor moiety. These reference compounds (1-S and 2-S) were obtained from 1-methoxy-4-methylbicyclo[2.2.2]octane[15] by Friedel–Crafts reaction with naphthalene catalysed by the boron trifluoride–diethyl ether complex.

$^1$H NMR spectra revealed that the products **2** from use of boron trifluoride were a mixture of two regioisomers linked at the 1 and 2 positions of the naphthyl moiety. The reference compound mixture could be separated into two pure isomers using reverse-phase HPLC. On the other hand, separation of the S–D dyad mixture **3** was difficult because the ferrocenyl moiety of the dyad is easily decomposed by oxygen in water, one of the



**Scheme 1**

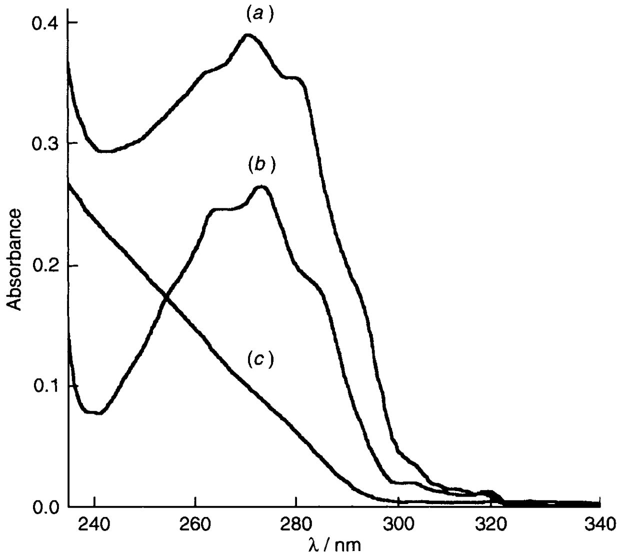


**Fig. 1** Absorption spectra of (*a*) S–D dyads (**3a**:**3b** = 1 : 1), (*b*) 1-methyl-4-(2-naphthyl)bicyclo[2.2.2]octane (2-S), (*c*) butylferrocene (Bu-Fc) in cyclohexane

solvents generally used for reverse-phase HPLC. Reverse-phase HPLC without oxygen is now under investigation. In addition, separation at the step of **2a** and **2b** may also prove useful. In the present work, separation of the S–D dyads was carried out with normal phase HPLC, although it is not an effective method for the separation of such a mixture of regioisomers. Two fractions with different molar ratios of isomers (1-naphthyl-S–D : 2-naphthyl-S–D = 2 : 1 and 1 : 1) were obtained by HPLC. The ratios of the 1- and 2-naphthyl isomers in these fractions were determined quantitatively by $^1$H NMR.[12]

The absorption spectra of the mixed S–D dyads (1 : 1) and the reference compound (2-S) in cyclohexane are shown in Fig. 1 together with the absorption spectrum of butylferrocene (Bu-Fc). The superposition of the spectra of 2-S and Bu-Fc is almost identical to the spectrum of S–D. The emission spectrum of the S–D dyads in cyclohexane shown in Fig. 2 is similar to those of the reference compounds, but the intensity of the former was two orders of magnitude lower than that of the latter. These spectral data indicate that the $\pi$-electronic structure of the naphthyl moiety was not changed by introduction of the ferrocene moiety, while the excited state of the naphthyl moiety was quenched effectively by the ferrocene donor moiety. A study of the dynamics of the S–D dyads and the reference compounds, using picosecond pulsed laser light, is currently in progress.

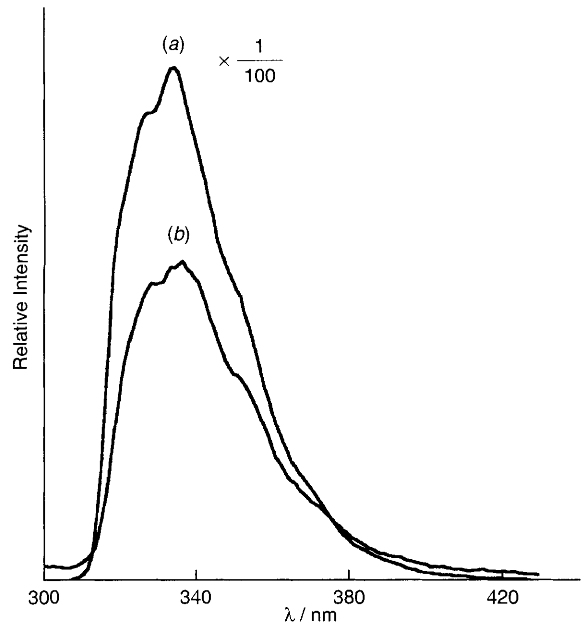


**Fig. 2** Fluorescence spectra of (*a*) 1-methyl-4-(2-naphthyl)bicyclo[2.2.2]octane (2-S), (*b*) S–D dyads (**3a**:**3b** = 1 : 1) in cyclohexane

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## Footnote

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