Synthesis of Novel Ferrocene–Naphthalimide Dyads†

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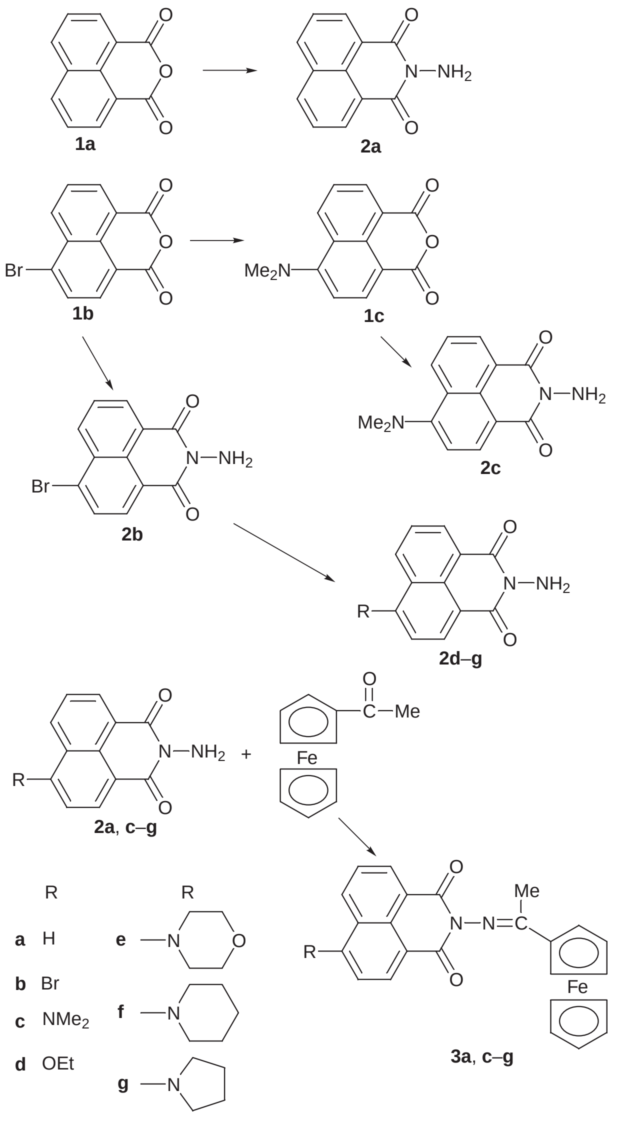
The synthesis of some novel ferrocene–naphthalimide dyads is described.

Naphthalimide derivatives are well known as brilliant greenish-yellow dyes for synthetic-polymer fibres. They generally show high fluorescence quantum yields, the emission band of which can be red-shifted by substitution at the 4-position. More recently, naphthalimide derivatives have also been used as supermolecular moieties in model compounds of the photosynthetic center for the study of photoinduced electron transfer.[1,2] As part of our efforts to synthesize photo-electrical switch molecules, we became interested in the preparation of ferrocene–naphthalimide dyads (NA–Fc). Ferrocene (Fc) is one of the most common organometallic subunits and a good electron donor and can be reversibly oxidized. Recently, a series of covalent linked fullerene–ferrocene dyads were reported and evidence was provided that the ferrocenyl center reduces the fullerene excited singlet states *via* intramolecular electron transfer.[3] Since Fc derivatives have oxidation potentials in the range 0.00–0.85 V (*vs.* SCE), there is an electron transfer from Fc to NA in the dyads (NA–Fc) and the fluorescence of NA is obviously quenched by such intramolecular electron transfer. When Fc is oxidized either electrochemically or chemically, intramolecular electron transfer from the oxidizing ferrocene (Fc^+) would be inhibited and the fluorescence of the NA moiety should be recovered. This type of dyad may find use in the area of molecular switches or molecular sensors.



Scheme 1 Synthetic route to ferrocene–naphthalimide dyads

To our knowledge, *N*-amino-1,8-naphthalimides condense readily with various ketones containing an α-methylene group to give the corresponding hydrazones[4,5] and the reaction can be effected in organic solvents in the presence of an acid catalyst. Compared with other acid condensation agents such as 4-toluenesulfonic acid and mineral acids, we found that glacial acetic acid was the most appropriate in this condensation reaction. Acetylferrocene was prepared by the known method.[6] The overall synthetic procedure is shown in Scheme 1. Suitable solvents for use in the above process include alcohols such as methanol, ethanol or isopropyl alcohol or chlorobenzene or even glacial acetic acid depending on the solubility of naphthalimide. The chemical structures of the dyads were confirmed by elemental analysis, ^{1}H NMR and MS.

Experimental

^{1}H NMR spectra were recorded on a Brucker AM-400 spectrometer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane. Mass spectra were obtained on Hitachi M80 instrument. Elemental analysis data were obtained on a Perkin Elmer 240c instrument. Reactions were monitored by thin-layer chromatography. All solvents were distilled prior to use. Acetylferrocene[6] and 1*H*-benz[*de*]isoquinoline-1,3(2*H*)-dione derivatives **2a**–**d** were prepared by known procedures,[7] while derivatives **2e**–**g** were prepared generally as follows: 2-amino-6-bromo-1*H*-benz[*de*]isoquinoline-1,3(2*H*)-dione **2b** and an excess of morpholine, pyrrolidine or piperidine were refluxed in 2-methoxyethanol for 2–4 h under nitrogen. On cooling a solid was deposited which was recrystallized several times from chlorobenzene to give orange or deep yellow needles.

General Procedures for Preparing Dyads.—Naphthalimide (1 mmol), acetylferrocene (1 mmol) and glacial acetic acid (0.1 mmol) in ethanol (50 cm^3) were refluxed for 4–8 h. The reaction was monitored by TLC and upon completion the solvent was evaporated and the residue purified by chromatography eluting with dichloromethane–acetone to afford an orange solid.

Compound **3a**. Yield 42%, mp 231–232 °C (decomp.); δ_H(CDCl$_3$): 2.13 (s, 3H, $=CCH_3$), 4.40 (s, 5H, unsubstituted cyclopentadiene), 4.51 (s, 2H), 4.93 (s, 2H) (substituted cyclopentadiene), 7.77 (m, 2H), 8.25 (d, $J = 2.20$ Hz, 2H), 8.65 (d, $J = 2.17$ Hz, 2H) (naphthalene ring); *m/z* 422 (M^+, 100%). Anal. Calc. for $C_{24}H_{18}FeN_2O_2$: C, 68.24; H, 4.26; N, 6.63. Found: C, 68.04; H, 4.30; N, 6.60%.

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Compound **3c**. Yield 52%, mp 238–240 °C; δ_H(CDCl$_3$): 2.10 (s, 3H, =CCH$_3$), 3.12 [s, 6H, N(CH$_3$)$_2$], 4.38 (s, 5H, unsubstituted cyclopentadiene), 4.48 (s, 2H), 4.90 (s, 2H, substituted cyclopentadiene), 7.13 (d, $J = 1.95$ Hz, 1H), 7.67 (m, 1H), 8.45 (d, $J = 2.0$ Hz, 1H), 8.55 (d, $J = 1.98$ Hz, 1H), 8.60 (d, $J = 1.70$ Hz, 1H) (naphthalene ring); *m/z* 465 (M$^+$, 100%). Anal. Calc. for $C_{26}H_{23}FeN_3O_2$: C, 67.09; H, 4.95; N, 9.03. Found: C, 66.71; H, 5.03; N, 8.70%.

Compound **3d**. Yield 26%, mp 245–247 °C (decomp.); δ_H(CDCl$_3$): 1.60 (m, 3H, OCH$_2$CH$_3$), 2.13 (s, 3H, =CCH$_3$), 4.34 (m, 2H, OCH$_2$), 4.39 (s, 5H, unsubstituted cyclopentadiene), 4.50 (s, 2H), 4.92 (s, 2H) (substituted cyclopentadiene), 7.04 (d, $J = 1.95$ Hz, 1H), 7.72 (m, 1H), 8.57 (m, 1H), 8.62 (m, 2H) (naphthalene ring); *m/z* 466 (M$^+$, 45%).

Compound **3e**. Yield 51%, mp 224–226 °C (decomp.); δ_H(CDCl$_3$): 2.12 (s, 3H, =CCH$_3$), 3.29 [m, 4H, N(CH$_2$–)$_2$], 4.03 [m, 4H, (–CH$_2$)$_2$O], 4.40 (s, 5H, unsubstituted cyclopentadiene), 4.51 (s, 2H), 4.94 (s, 2H) (substituted cyclopentadiene), 7.24 (d, $J = 2.0$ Hz, 1H), 7.73 (m, 1H), 8.47 (m, 1H), 8.58 (m, 1H), 8.64 (m, 1H) (naphthalene ring); *m/z* 507 (M$^+$, 44%).

Compound **3f**. Yield 34%, mp 249–251 °C (decomp.); δ_H (CDCl$_3$): 1.72 (m, 2H, CH$_2$), 1.88 (m, 4H, NCH$_2$CH_2), 2.10 (s, 3H, =CCH$_3$), 3.24 [m, 4H, N(CH$_2$–)$_2$], 4.38 (s, 5H, unsubstituted cyclopentadiene), 4.48 (s, 2H), 4.90 (s, 2H) (substituted cyclopentadiene), 7.18 (d, $J = 1.95$ Hz, 1H), 7.68 (m, 1H), 8.40 (m, 1H), 8.52 (m, 1H), 8.60 (m, 1H) (naphthalene ring); *m/z* 505 (M$^+$, 100%).

Compound **3g**: Yield 32%, mp 243–245 °C (decomp.); δ_H (CDCl$_3$): 2.09 (m, 7H, =CCH$_3$, NCH$_2$CH_2), 3.78 [m, 4H, N(CH$_2$)$_2$], 4.38 (s, 5H, unsubstituted cyclopentadiene), 4.46 (s, 2H), 4.90 (s, 2H) (substituted cyclopentadiene), 6.80 (d, $J = 2.10$ Hz, 1H), 7.53 (m, 1H), 8.43 (m, 1H), 8.59 (m, 2H) (naphthalene ring); *m/z* 490 (M$^+$, 100%).

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