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N-Ferrocenyl Naphthalimides: Synthesis, Structure, and Redox Chemistry

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A family of *N*-ferrocenyl-1,8- and *N*-ferrocenyl-2,3-naphthalimide and *N*,*N*-diferrocenyl-1,4,5,8-naphthaldiimide complexes has been prepared by reaction of naphthalic anhydrides or naphthalimide anions with a ferrocenylamine. The *N*-ferrocenyl substituents are 1,8 (Fc, $FcCH_2$, FcCHMe, $Fc(CH_2)_{11}$), 1,4,5,8 (Fc, $FcCH_2$, FcCHMe, $Fc(CH_2)_{11}$), 3-NO_2-1,8- ($FcCH_2$, FcCHMe), 4-NO_2-1,8 (Fc, $FcCH_2$, FcCHMe, $Fc(CH_2)_{11}$, 1,1′-$BrFcCH_2$), 4-Br-1,8 ($FcCH_2$, $Fc(CH_2)_{11}$), and 2,3 (Fc, $FcCH_2$, FcCHMe, $Fc(CH_2)_{11}$). A novel stacking aggregation occurs with the 1,4,5,8-Fc and -$FcCH_2$ derivatives, and intramolecular donor−acceptor charge transfer is evident in the aggregate. Steric hindrance precludes this aggregation in other 1,4,5,8 analogues. An X-ray structure of the 3-NO_2-1,8 derivative shows an L-shaped molecule which packs in a columnar array. Micelle formation occurs with long-chain derivatives. The electronic spectra and electrochemistry show that the *N*-ferrocenyl substituents do not perturb the energy levels of the fluorophore, although emission is quenched. Coupling of the 4-Br compounds with ethynylferrocene provides direct communication of the redox switch to the fluorophore.

Introduction

Naphthalimide derivatives have photophysical properties which have been widely used as brilliant yellow dyes in synthetic fiber technology,[1] in biomedical science as intracellular markers (particularly Lucifer dyes),[2] as optical brighteners,[3] and as models for photoinduced electron transfer.[4] They are good electron acceptors, and those with an electron acceptor on the aromatic ring and a donor at the end of the alkyl chain have been shown to intercalate with DNA by donor−acceptor interactions[5] and to have antineoplastic properties.[6] The lowest excited state is predominately π,π^* in character, and their photochemistry is sensitive to the position of the dicarboxyimide group and solvent. 1,2- and 2,3-naphthalimides fluoresce with good to high quantum yields, but an efficient intersystem crossing process deactivates the singlet excited state for 1,8- and 1,4,5,8-naphthalenediimides,[7] although the acceptor properties of diimides have been exploited in materials science.[8] The dependence of quantum yield on other groups on the naphthalimide ring and the N-substituent and correlation with theoretical calculations have been the subject of a number of studies.[7,9] For example, emission is reduced by a nitro substituent, although bioreduction restores the fluorescence,[10] and competition, which exists between photoinduced electron transfer and emission when there is an amino substituent, will quench fluorescence.[11] Aggregation leading to excimer formation[7,9,12] and CT complexation[13] through π interactions are also well-understood.

Our interest in naphthalimides is as the fluorophore component in electroluminescent organometallic molec-

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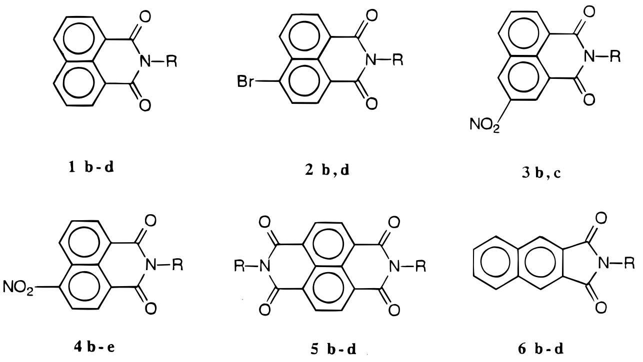
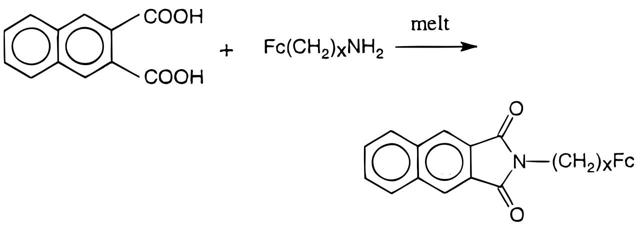
ular switches and bioprobes. Organometallic substituents might be expected to shut down the fluorescence from naphthalimides, but the parameters which modulate the quantum yields in this type of molecule have not been elucidated. Whether there is a critical "distance factor" or dependence on oxidation state has not been established, and it may be possible to use specific electronic and structural features of organometallic naphthalimide derivatives to tune naphthalimide emission. An investigation of electroluminescent materials containing a naphthalimide fluorophore linked to an organometallic electrophore (ferrocene and/or $CCo_3(CO)_9$) was therefore undertaken. These electrophores have well-behaved tunable redox couples[14,15] (particularly the cluster, which can be tuned over a 0.0−1.4 V cathodic and 0.0−1.2 V anodic range[16]) and give an opportunity to study the photophysics of species other than 18-electron ones. Our interest in these as modules in molecular switches and in bioscience also stems from the demonstration that conformationally different excited states can arise through hindered rotation in *N*-aryl compounds[17] and *N*-phenylnaphthalimides appear to have both long- and short-wavelength emission.[18] Metallocene and metal clusters with their delocalized bonding could be analogous to the phenyl derivatives, and they have the capacity to adopt a variety of orientations in the solid state. Ferrocene is an efficient quencher of triplet excited states, often at diffusion-controlled rates, where a donor triplet state lies above that of ferrocene at approximately 179 kJ mol^{-1}. Nevertheless, aggregation, CT complexation, and excimer formation may well influence the photophysics in different ways when there is an N-organometallic substituent, and these processes may be dependent on the redox potential of the N-substituent—with the consequent potential to act as molecular switches. Reduction of the organometallic naphthalimide opens up another pathway for aggregation via stacking of the imide anion radicals. Tian and co-workers[19] have recently reported the preparation of several imide−ferrocenes with isoquinoline substituents on the naphthalimide ring. In this paper we report a family of *N*-ferrocenylnaphthalimides and *N*,*N*′-diferrocenylnaphthalenediimides, particularly those with a 1,8 profile, as their radicals have high electron density at the C-4 position, and we also present a preliminary investigation of their electrochemical and spectroscopic properties. Water-soluble derivatives, detailed photophysics, ESR spectroscopy, and the surfactant and neuroprobe properties of ferrocenylnaphthalimides will be covered in succeeding papers.[20]

Chart 1



b $FcCH_2$ **c** FcCHMe* **d** $Fc(CH_2)_{11}$ **e** 1′-BrFcCH $_2$

Scheme 1



6 b-d

Results and Discussion

The direct reaction between the naphthalic anhydride and the appropriate ferrocenylamine in ethanol or isobutyl alcohol gave the *N*-(ferrocenylalkyl)-1,8-naphthalimides and *N*,*N*′-bis(ferrocenylalkyl)-1,4,5,8-naphthaldiimides shown in Chart 1. Yields were dependent on the basicity of the ferrocenyl substituent and its steric requirements. Those with the longer methylene chain, **1d**−**5d**, gave good yields. Despite the high basicity of the parent amine,[21]$FcCH(Me)NMe_2$ derivatives were formed in low yields, presumably because of the steric hindrance from the α-Me group. Analogous *N*-(ferrocenylalkyl)-2,3-naphthalimides **6** were prepared directly from 2,3-naphthalenedicarboxylic acid (Scheme 1).

Although derivatives with the *N*-ferrocenyl group directly bound to the imide could be made by the above route, the low basicity of $FcNH_2$ resulted in very low yields. To overcome this problem, a convenient synthesis was used whereby a copper naphthalimide[22] was reacted with bromoferrocene in boiling picoline to give the *N*-ferrocenylnaphthylimides **1a** and **4a**−**6a** (Scheme 2).

An alternative strategy using modified Gabriel syntheses was also explored as a potential route to bis(ferrocenyl) derivatives; this would obviate the difficult preparation of bis(ferrocenyl)amines. An example of this method is the reaction of potassium 1,8-naphthalimide[23] with a bromoalkylferrocene, giving high yields of **1d** (Scheme 3).

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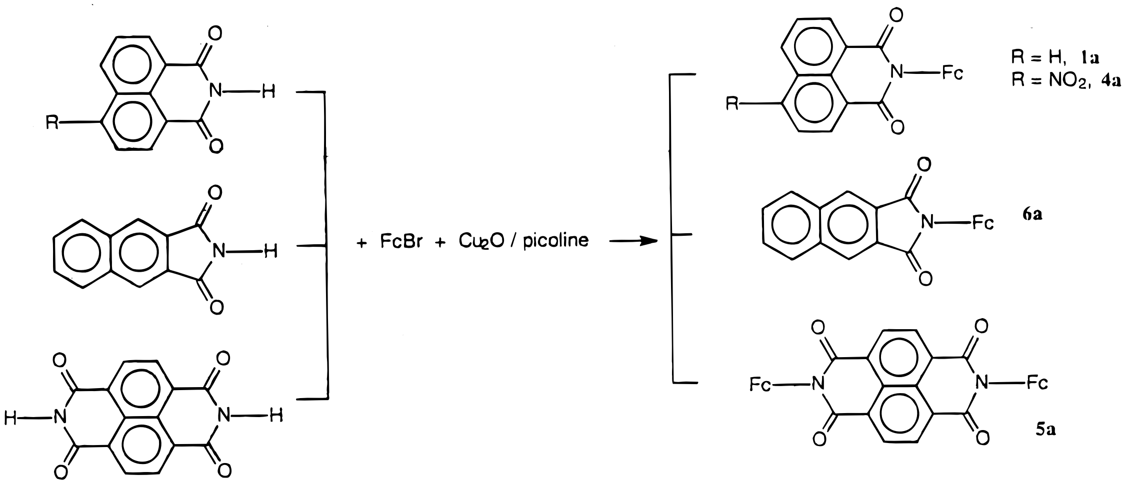
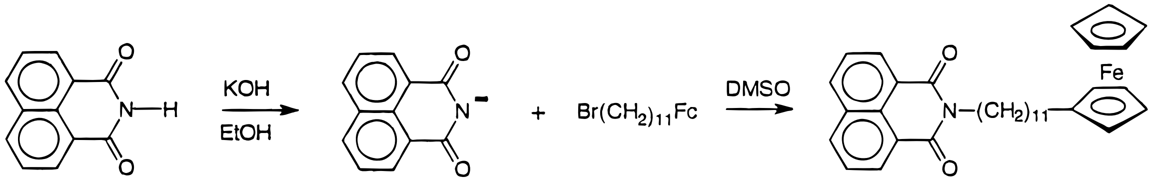
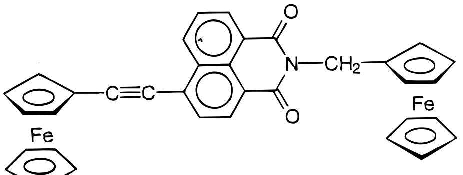
Scheme 2



Scheme 3



Ferrocenylnaphthalimides with additional functional groups as in **2**−**4** allow for the construction of arrays in which communicating links to both the naphthalene ring and imide can be introduced. Thus, the CuI/(PPh$_3$)$_2$-PdCl$_2$-catalyzed coupling of **2b** with ethynylferrocene gave **7**, in which one ferrocenyl redox center is in direct communication with the fluorophore via the alkyne link.



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All compounds were characterized by microanalysis, MS, NMR (except **5a**,**b**; vide infra), and electronic spectra. The *N*-(Me)CHFc derivatives **1c** and **3c**−**6c** were prepared as racemates. In general, the *N*-ferrocenylnaphthalimides were yellow to brown crystalline solids, soluble in chlorinated and aromatic solvents but poorly soluble in alcohols. The exceptions were **4**, which was green, the insoluble **5a**,**b** (see below), and the long-chain Fc(CH$_2$)$_{11}$ oils **1d** and **2d**. The last examples exhibited surfactant-like behavior, and their properties in organized microheterogeneous media and vesicle formation will be the subject of further study.

Aggregation of *N*-Ferrocenyl-1,4,5,8-naphthaldiimides. Compounds **5a,b** warrant special consideration because they are a dark *green* color with an additional band at 630 nm in the reflectance absorption spectra compared to the soluble compounds. Furthermore, they are *insoluble* in all solvents. There is chromatographic evidence for a soluble form during the reaction, but on workup and concentration the aggregation process is irreversible. It is well-known that the solubility of simple alkyl 1,4,5,8-naphthaldiimides is often very low.[24] Nonetheless, the fact that the FcCH(Me) and Fc(CH$_2$)$_{11}$ analogues are very soluble in organic solvents and are not green suggests there is an underlying factor inducing the aggregation. We suggest that aggregation of the 1,4,5,8 ferrocenyl derivatives is caused by a strong π−π stacking interaction[25] which in **5c** is prohibited by the pendant α-Me group and in **5d** by the amphiphilic tail. There appears to be little perturbation of the naphthalimide fluorophore in **5a**,**b**, as their π−π^* transitions in the reflectance spectra are at the same energy as for the soluble analogues (Table 2). What is most significant is the electronic transition at 630 nm characteristic of ferrocenium compounds, giving the green color. Thus, aggregation appears to give a stack in which partial intramolecular charge transfer takes place giving both Fe(II) and Fe(III) centers. This is a novel situation for a neutral naphthalimide, and a detailed examination of the aggregation process, and the solid-state properties of the aggregates, is currently underway. Oxidation of a suspension of **5a**$^+$ and **5b**$^+$ in CH$_2$Cl$_2$ with NO$^+$BF$_4^-$ gives the deep blue Fe(III) analogues, which are still insoluble. This is surprising, as it was anticipated that Coulombic repulsion between the ferrocenium centers would dislocate the aggregate.

Crystal Structure of 3b. Models suggested that steric interactions between individual ferrocenylnaphthalimide molecules would impact on their ability to stack or form dimers. An X-ray single-crystal study of **3b** was therefore undertaken in order to obtain the important steric parameters for an individual molecule.

In the structure of **3b** (Figure 1) the naphthalimide skeleton is essentially coplanar, with the 3-nitro group only twisted slightly out of the plane of the naphthalene

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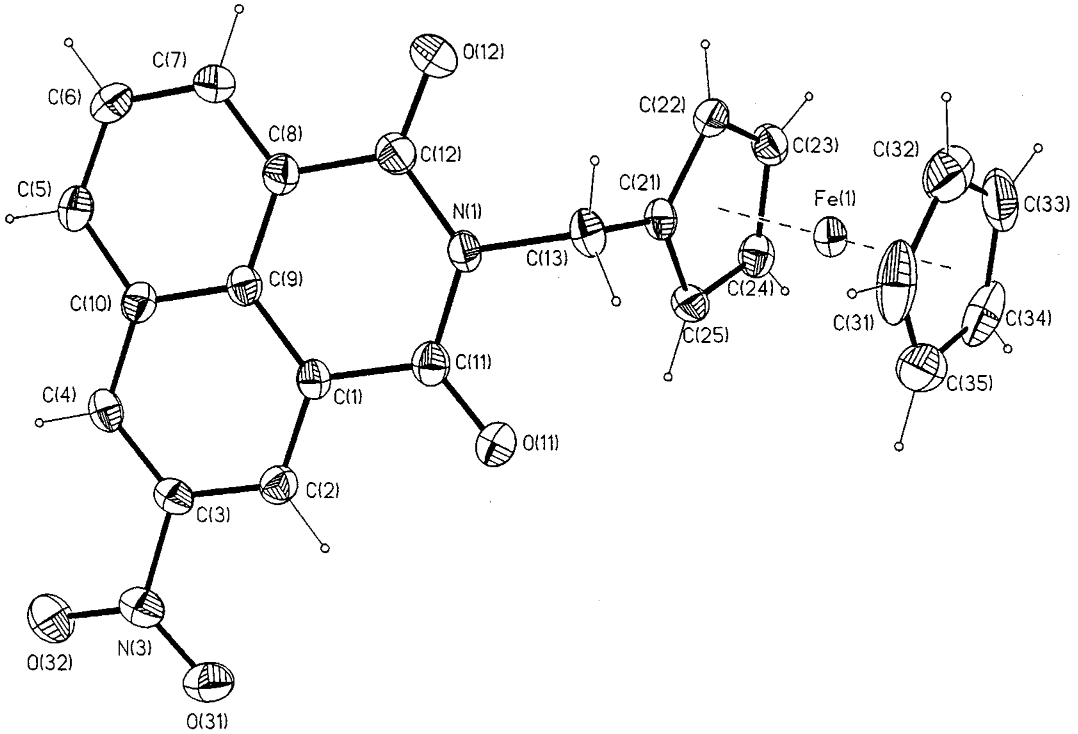

Figure 1. Structure of one molecule of compound **3b** showing the atom-numbering scheme. For clarity, numbering is shown only for the first two C atoms of the consecutively numbered cyclopentadiene rings.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3b

C(1)−C(2)	1.377(3)	C(6)−C(7)	1.414(3)
C(1)−C(9)	1.420(3)	C(7)−C(8)	1.381(3)
C(1)−C(11)	1.497(3)	C(8)−C(9)	1.419(3)
C(2)−C(3)	1.405(3)	C(8)−C(12)	1.489(3)
C(3)−C(4)	1.373(3)	C(9)−C(10)	1.431(3)
C(3)−N(3)	1.481(2)	C(11)−N(1)	1.398(2)
N(3)−O(31)	1.232(2)	C(11)−O(11)	1.226(2)
N(3)−O(32)	1.231(2)	C(12)−O(12)	1.223(2)
C(4)−C(10)	1.423(3)	N(1)−C(12)	1.411(3)
C(5)−C(6)	1.373(3)	N(1)−C(13)	1.496(2)
C(5)−C(10)	1.427(3)	C(13)−C(21)	1.507(3)
O(11)−C(11)−N(1)	121.65(18)	C(12)−N(1)−C(13)	118.06(16)
O(11)−C(11)−C(1)	121.85(18)	O(12)−C(12)−N(1)	120.14(19)
N(1)−C(11)−C(1)	116.49(18)	O(12)−C(12)−C(8)	122.6(2)
C(11)−N(1)−C(12)	125.27(17)	N(1)−C(12)−C(8)	117.22(17)
C(11)−N(1)−C(13)	116.61(17)	N(1)−C(13)−C(21)	112.43(16)

Table 2. Spectral and Electrochemical Data[a]

	electronic spectrum/nm[b]			$E_{1/2}$/V[c]		
			Fc	**A**	**B**	**C**
1a	333	347	452	0.57	−1.4	
1b	333	349	438	0.59	−1.1	
1c	333	349	438	0.58	−1.2	
1d	334	349	439	0.48	−1.1	
2b	343	358	438	0.60	−1.1	
2d	343	358	438	0.48	−1.1	
3b	318	332	438	0.61	−0.9	
3c	318	333	438	0.60	−0.9	
4b		350	440[d]	0.62	−0.58[f]	−0.86
4c		350	440[d]	0.60	−0.58[f]	−0.88
4d		352	440[d]	0.50	−0.54[f]	−0.83
4e		348	440	0.76	−0.53[f]	−0.83
5a[e]	360	390	445			
5b[e]	368	389	440			
5c	361	382	438	0.59	−0.60	−1.1
5d	359	380	440	0.49	−0.58	−1.0
6a	342	357	450[d]	0.64	−1.4	
6b	342	358	421	0.63	−1.2	
6c	342	358	420[d]	0.62	−1.1	
6d	342	358	438	0.49	−1.4	
7	355	377	505	0.58 (0.71)	−1.1	

[a] In dichloromethane. [b] At 20 °C. Extinction coefficients are available from the authors; data for spectra in methyl cyanide are similar to those in dichloromethane. [c] $E^{1/2}$ values, from square-wave voltammetry vs decamethylferrocene, Conditions: Pt; 20 °C; 200 mV s^{-1}. [d] Shoulder on rising absorption due to naphthalimide. [e] Reflectance spectrum; additional bands at 630 nm. [f] For comparison, *N*-phenyl-4-nitro-1,8-naphthalimide: −0.53, −0.82 V.

ring (interplanar angle 7.7(3)°). The ferrocenyl methylene carbon C(13) joined at the imide N atom is also coplanar, giving a “flat” feature. This coplanarity of the methylene then forces the ferrocenyl moiety to minimize interactions with the CH$_2$ link by orienting the N(1)−C(13)−C(21) plane such that it is approximately perpendicular to the dicarboximide ring plane (interplanar angle 88.2(1)°) (Figure 2). The cyclopentadienyl rings are, unexpectedly, inclined at angles of 70.12(5)° (C(21)···C(25)) and 70.17(6)° (C(31)···C(35)) to the overall naphthalenedicarboximide ring plane. Bond lengths and angles in the naphthalenedicarboximide system (Table 1) are unremarkable and compare well with those found in systems with both aliphatic[26,27] and aromatic[28,29] substituents on the imide nitrogen. The N(1)−C(13) bond length of 1.496(2) Å is also similar to those found in the related *N*-ethyl[26] and *N*-butyl[27] compounds. Although the intervening methylene group precludes

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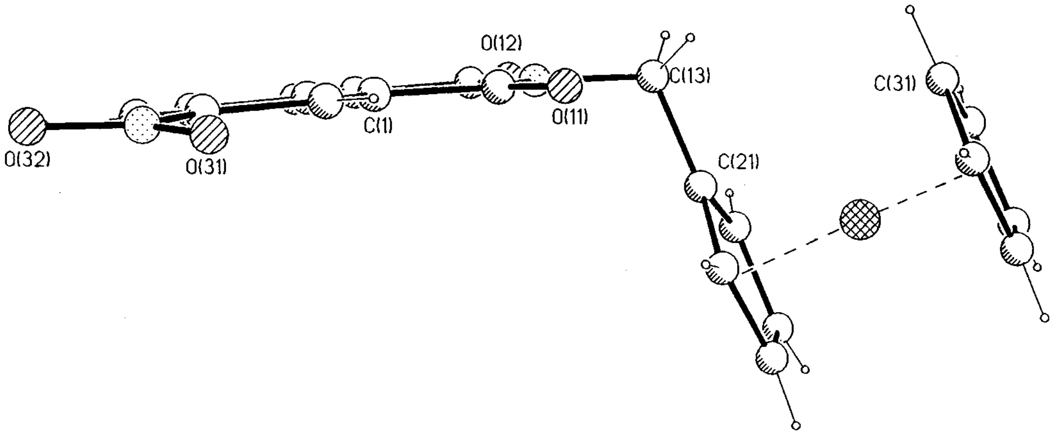


Figure 2. View of **3b** 90° to the naphthalene ring.

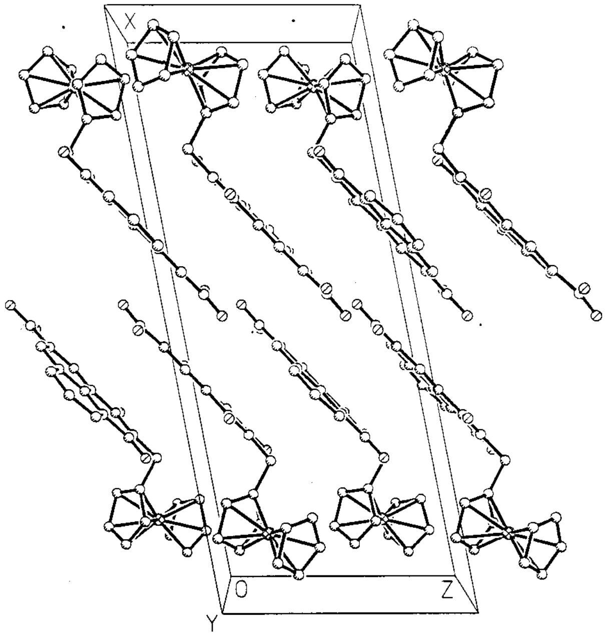


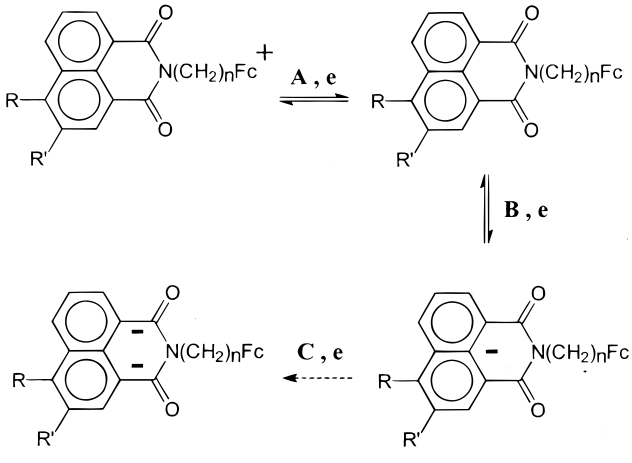
Figure 3. Packing of **3b** in the lattice.

the possibility of direct electronic interaction between the naphthalene acceptor and ferrocenyl donor, a through-space donor−acceptor interaction cannot be ruled out.

Because of the coplanarity of the naphthalimide core the solid-state structure (Figures 2 and 3) can be stabilized by columnar interactions involving the naphthalenedicarboximide units. Similar interactions have been noted previously for dicarboximide systems.[28,29] Molecules stack in a transverse fashion along the *a* axis, with interplanar distances in the range 3.32−3.37 Å. This is well within the range required for $\pi-\pi^*$ interactions. Packing in **3b** is facilitated by the arrangement of adjacent pairs of molecules in an obverse fashion with respect to the columnar axis. This places the bulky ferrocenyl moieties on the periphery of the columnar network. In the column the 3-nitro substituents are related to each other by a pseudo 2-fold axis, generating an ABAB pattern; the shortest N3···N3 contact is approximately 3.58 Å.

The implications from the **3b** structure for the aggregation of the ferrocenyldiimides **5a,b** via $\pi-\pi^*$ stacking are significant. Clearly, for **5a**, there is only one possibility for stacking where the Fc terminii have minimal contact; this is where the Fc groups are alternating at 90° to each other along the long axis of the stack. There is more freedom for a alkylferrocenyl group, but a methyl substituent on the α-carbon would stop face-to-face stacking, in agreement with experiment.

Scheme 4



R' = H R = H, NO_2, Br
R' = NO_2 R = H

Redox Chemistry. The ferrocenyl derivatives **1**−**6** all display both oxidation and reduction processes in their cyclic and square-wave voltammetry (Scheme 4).

One-electron [Fc^+/Fc] oxidation (**A**; Figure 4) is chemically and electrochemically reversible in dichloromethane. A $\Delta E_{1/4-3/4}$ value of 0.59 mV indicates that **A** for **5c,d** (Figure 4b) constitutes two one-electron processes occurring independently at each ferrocenyl center. This was confirmed by comparing the peak to peak currents in a voltammetry run with an equimolar amount of decamethylferrocene. The absence of communication between these redox centers is not unexpected, as the HOMO for the naphthalene core is of different symmetry (a_2) to that of the carboximide-ferrocenyl fragment (b_1) and there is a node at the *N* atom.[7,18] Unfortunately, the insolubility of **5a**,**b**, where communication was more likely, prohibited any electrochemical studies.

$E_{1/2}$(**A**) for the shorter chain compounds **a**−**c** are in the range 0.60 ± 0.3 V vs decamethylferrocene, ir-

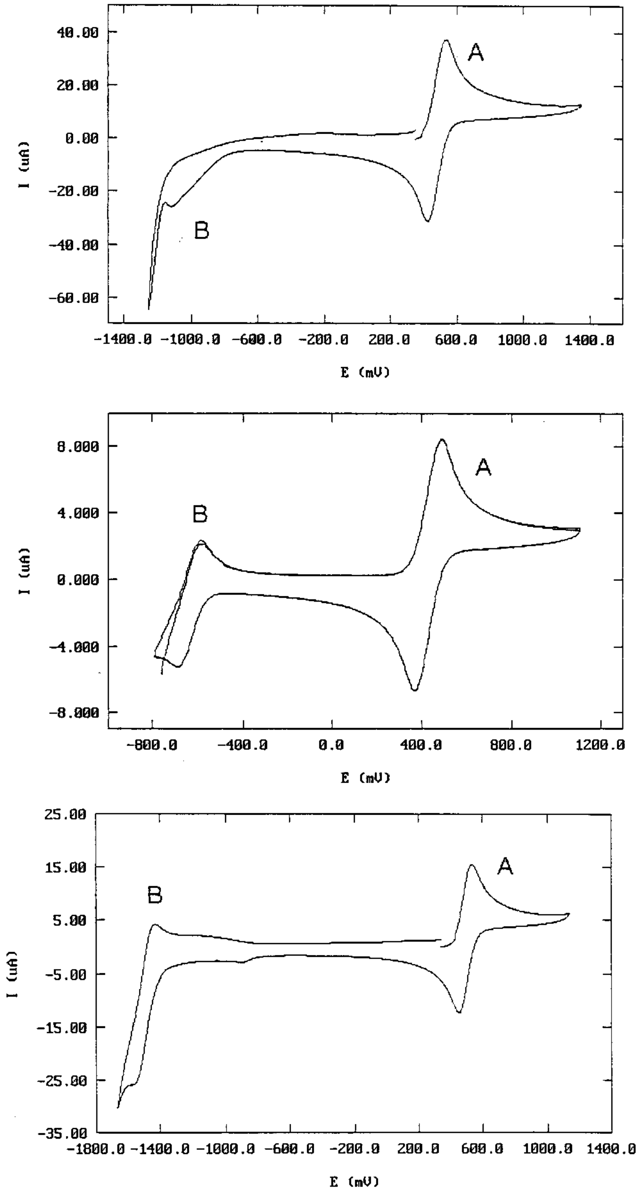


Figure 4. Cyclic voltammograms (CH_2Cl_2, 200 mV s^{-1}, Pt, 20 °C): (a, top) **1d**; (b, middle) **5d**; (c, bottom) **6d**.

respective of the position of the imide substituent. These potentials are slightly anodic of $E_{1/2} = 0.55$ V for ferrocene, as expected for a naphthalimide group acting as an electron-withdrawing group. Insulation of the ferrocenyl moiety from the naphthalimide by the long alkyl chain in the amphiphilic derivatives **1d**−**5d** shifts $E_{1/2}$(**A**) cathodically to 0.49 V, a potential identical with that of the ferrocenylamine.[21] These data confirm that neither the naphthylimide moiety nor oxidation of the amphiphilic molecules, which generates a polar head-group, has anything other than a Coulombic effect on the redox properties of the ferrocenyl substituent.

The ethynylferrocene complex **7** has two oxidation processes at 0.58 V (**A**) and 0.71V (**A′**) (Figure 5). The first, which is essentially the same as **A** for the parent **2d**, is assigned to the Fc(imide) group and **A′** to oxidation of the 4-ethynylferrocene substituent (Scheme 5)—$E_{1/2}$ for ethynylferrocene is 0.69 V, and the absence of any shift to positive potentials from the Coulombic effect of the (imide)CH_2Fc^+ unit on the oxidation of C≡CFc in 7^+ reinforces the insulating character of the imide nitrogen.

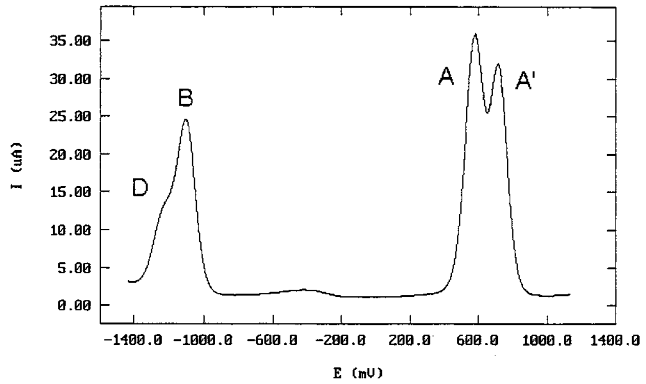


Figure 5. Square-wave voltammogram of **7** (CH_2Cl_2, 200 mV s^{-1}, Pt, 20 °C).

In agreement with other data for naphthalimides[12,23,30,31] the *N*-(ferrocenylalkyl)naphthalimides undergo a reduction **B** in dichloromethane with variable chemical reversibility and transfer of electrons (Table 2, Figure 4). It is expected from the calculated HOMO and LUMO configurations that the potential of the first reduction step will be dependent on the substituent on the naphthalene ring but little influenced by the N-substituent because of the node at the imide nitrogen. Thus, *E*°(**B**) decreases in the order **1** < **2** < **3** < **4** due to the −I effect of the Br and NO_2 groups and there is a linear correlation with the Hammett substituent constants. These potentials are similar to those reported for other 1,8-naphthalimides.[12,23,30,31] The *N*-ferrocenyl-CHR substituent has little influence on *E*°(**B**). However, when the ferrocenyl group is bonded directly to the imide nitrogen, *E*°(**B**) shifts cathodically by 0.3 V (cf. **1a**,**b**). This large cathodic shift might be interpreted as a change in HOMO/LUMO character, but calculations show this is not the case, and it is simply an inductive effect of the ferrocene moiety. It is often assumed that **B** for simple naphthalimides is a reversible one-electron process involving the radical anion. However, for the *N*-ferrocenylnaphthalimides **B** is certainly not a simple step, as the number of electrons transferred, referenced against the internal *N*-ferrocenyl group, varies from one for **3b** to approximately two for **6d** (see Figure 4). Likewise, the kinetics of the ECE process is variable. **B** for **7** is more complex again, with a rapid chemical reaction at **B** giving rise to the relatively stable species **D**, which is reduced at nearly the same potentials as **B** (Figure 5). The most stable radical anions (with the exception of **4c**) are those of the diimides **5c**,**d** (Figure 4b). Evidence for self-association is often found in the electrochemistry of naphthalimide radical anions, and although this cannot be ruled out, there was no indication of precipitation or concentration-dependent behavior with the ferrocenyl derivatives.

There is, normally, a second, often multielectron, chemically irreversible step **C** cathodic of **B**. The exceptions to this pattern are the 4-nitro derivatives **4**. For these, the two reversible one-electron processes **B** and

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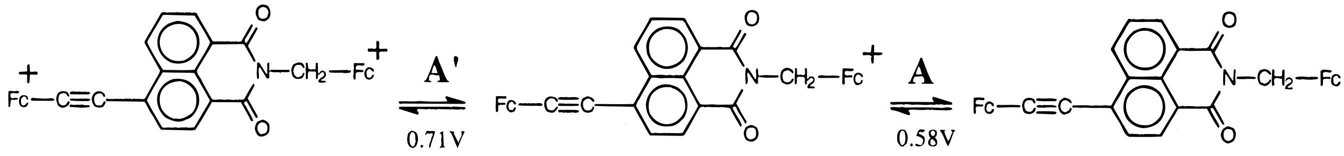
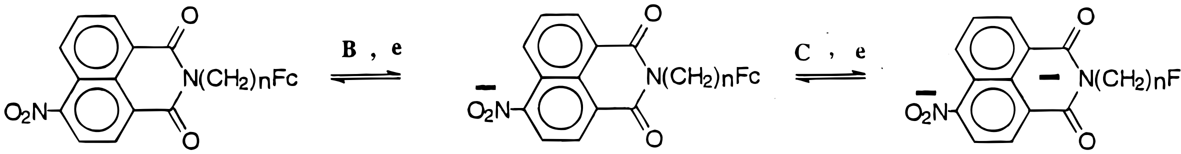
Scheme 5



Scheme 6



C (sweep rates 20−1000 mV s^{-1}) are observed in CH_2Cl_2, CH_3CN, and DMF (Figure 6). Extended Huckel-MO calculations show that the spin density of the radical anion $\mathbf{4}^{\bullet-}$ is located on the *nitro* group, and this is confirmed by the ESR spectra. In contrast, the spin density in the dianion $\mathbf{4}^{2-}$ is centered on both the nitro group and the fluorophore (Scheme 6). The lifetime of the dianion $\mathbf{4b}^{2-}$ is short on the electrochemical time scale, whereas $\mathbf{4c}^{2-}$ is long-lived. The greater stability of the sterically congested derivative $\mathbf{4c}^{2-}$ suggests that the ECE pathway for the dianions involves bimolecular reactions. The evidence for the location of the spin density in the 4-nitro derivatives is unequivocal. It is therefore surprising that similar redox chemistry is not found for the 3-NO_2 derivatives, as calculations show that the spin density for the radical anions $\mathbf{3}^{\bullet-}$ also resides on the nitro group.

Electronic Spectra. 1,2-, 2,3-, and 1,8-naphthalimides and 1,4,5,8-naphthaldiimides have[7,9,10,18] one $\pi-\pi^*$ transition with associated vibronic progressions, in the range 430−330 nm. Broad, structureless bands are seen at higher energies. The long-wavelength $\pi-\pi^*$ transition involves a HOMO centered on the naphthalene skeleton and the LUMO centered on the carboximide substituent. Its vibronic structure is well-defined for 1,8 derivatives, indicating that there is a narrow distribution of vibrational states in the electronic transitions and constant geometry in the relaxed excited and ground states. Data for the *N*-ferrocenylnaphthalimides are given in Table 2. Derivatives **1** display the typical naphthalimide $\pi-\pi^*$ absorption in CH_3CN at ∼349 nm and a ferrocenyl transition at ∼440 nm (Figure 7). In keeping with the small dipole change in the transitions they are insensitive to solvent polarity. Derivatives **5c**,**d** and **6** display similar features in their absorption spectra, with the smaller HOMO−LUMO energy gaps being reflected in the lower $\pi-\pi^*$ energies. It is noteworthy that the ferrocenyl transition is consistently around 440 nm for **1**−**6**, showing that there is little frontier orbital interaction between the donor and acceptor. This is compatible with the existence of a node at the N-atom of the carboximide and the data on other imides.[7,9] Oxidation of the ferrocenylnaphthalimides with $NO^+BF_4^-$ or I_2 gave the dark green-blue ferrocenium species $\mathbf{1}^+$−$\mathbf{6}^+$. There is relatively little change in the energy of the $\pi-\pi^*$ bands upon oxidation, and the typical ferrocenium band at ∼630 nm was observed in the electronic spectra.

The $\pi-\pi^*$ band profile in the 260−400 nm range is a fingerprint for the naphthalimide substitution pattern, and there are significant differences in energy and profile of **1**−**4**. Derivatives **2** have the same structured $\pi-\pi^*$ profile as **1** but with a red shift, a consequence of the reduced electron density in the HOMO from the −I effect of the Br group. However, the 3-NO_2 derivatives **3**, while retaining a weak ill-defined structured $\pi-\pi^*$ feature at 331 nm, show a blue shift from **1** and a strong structureless band at 280 nm. At this stage it is uncertain whether the latter is a nitro or naphthalimide band. All 4-NO_2 derivatives **4**, on the other hand, have only a weak shoulder at 260−285 nm (the energy of which is dependent on the ferrocenyl group) and a broad (∼34 nm half-bandwidth) structureless band at ∼350 nm. The latter feature is insensitive to solvent. The energy levels of **4a**−**e** are clearly different from those of **1a**−**d**. This is consistent with work on 4-NO_2-

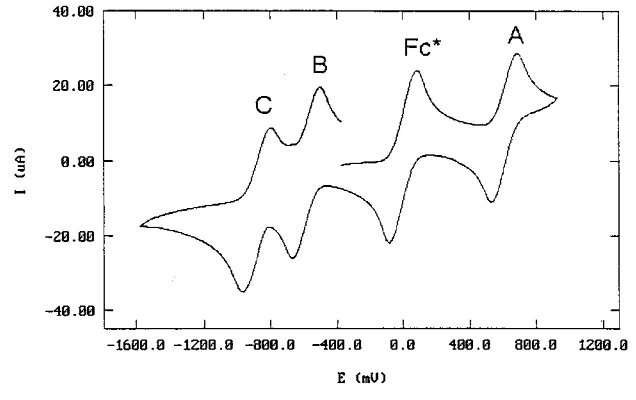


Figure 6. Cyclic voltammogram of **4c** (CH_2Cl_2, 200 mV s^{-1}, Pt, 20 °C).

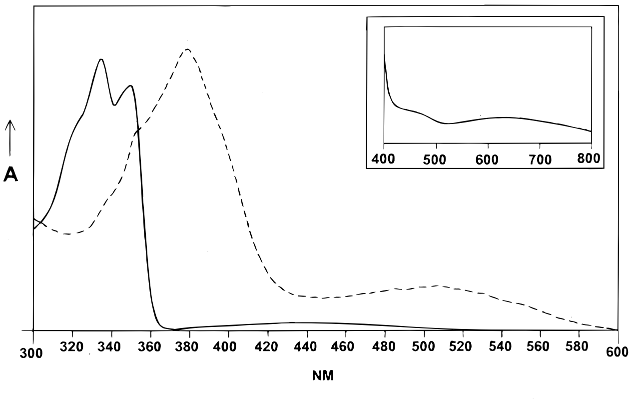


Figure 7. Electronic spectra in CH_2Cl_2 (∼10^{-4} M): (—) **1d**; (- - -) **6d**. Inset: reflectance spectrum of **5b**.

naphthalimide radical anions, where it is found[30] that experimental ESR spectra do not agree with theory. Detailed assignments based on our theoretical calculations and their correlation with spectral data will be given elsewhere.[20]

The electronic spectrum of **7** is particularly interesting, as there are marked red shifts in both the $\pi-\pi^*$ transitions and "ferrocenyl" bands and a large increase in extinction coefficients (Table 2, Figure 7). It is likely that the weaker *N*-ferrocenyl band is hidden under the broad 505 nm band. which we ascribe to a transition having both FcC≡C and fluorophore character. Shifts of the ferrocenyl transition to lower energy occur only when there is conjugation between a ferrocene unit and an electron-withdrawing substituent, and the equivalent band for ethynylferrocene is at 442 nm. The existence of an intense 505 nm band in **7** is strong evidence that there is a significant perturbation of the ferrocenyl frontier orbitals. Fluorescence spectra of **7** suggest that that the fluorophore is quenched.

Conclusion

The family of *N*-(ferrocenylalkyl)naphthalimides described in this paper provides a platform for the development of ferrocenylnaphthalimides for use in neuroscience, intercalation studies of DNA, and molecular switches. Extension into molecular architectures with redox-switched bifluorophores, and cluster derivatives, is clearly possible via the 4-Br compounds. Water solubility can be achieved via sulfonated derivatives akin to the Lucifer dyes.[20] A node at the *N*-imide atom acts as an effective insulator of the *N*-ferrocenyl redox switch from the naphthalimide fluorophore, whereas a switch linked to the naphthalene ring through an unsaturated group is perturbed. Since the fluorophore is quenched by an *N*-ferrocenyl substituent at the nodal imide, the quenching mechanism must be energy transfer rather than electronic. Significant $\pi-\pi$ stacking in naphthalenediimides is engendered by the addition of the electron-donor ferrocenyl group. What intramolecular charge-transfer mechanism causes partial oxidation in the aggregate is uncertain at present. It will be important to find at which point the change from aggregate to monomer to micelle structure occurs, as aggregation−monomer electronic switching is, in principle, feasible with this system.

Experimental Section

Solvents were dried and distilled by standard procedures, and all reactions were performed under nitrogen. Naphthalic anhydrides, 1,8-naphthalimide, 2,3-naphthalenedicarboxylic acid, and dicarboximide were purchased from Aldrich. Potassium naphthalimide,[32] $Fc(CH_2)_{11}Br$,[33] and aminoferrocenes $FcNH_2$,[34] $FcCH_2NH_2$,[35] $FcCHMeNH_2$[36] were prepared by literature methods. Other commercial reagents were used as received. IR spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR spectrometer, NMR on a Varian VXR 300 MHz or Gemini 200 MHz spectrometer (^1H NMR were referenced to $CDCl_3$), and electronic spectra on Jasco V 550 UV−vis spectrophotometers; $\pi-\pi^*$ band maxima were obtained from convoluted spectra. Microanalyses were carried out by the Campbell Microanalytical Laboratory, University of Otago. Mass spectra were recorded on a Kratos MS80RFA instrument with an Iontech ZN11NF atom gun. Cyclic and square-wave voltammetry in CH_2Cl_2 was performed for all compounds using a three-electrode cell with a polished Pt disk (2.27 mm^2) as the working electrode; solutions were $\sim10^{-3}$ M in electroactive material and 0.10 M in supporting electrolyte (triply recrystallized $TBAPF_6$). Data were recorded on an EG & G PAR 273A computer-controlled potentiostat. Scan rates of 0.05−1 V s^{-1} were typically employed for cyclic voltammetry, and for Osteryoung square-wave voltammetry, square-wave step heights of 1−5 mV and a square amplitude of 15−25 mV with a frequency of 30−240 Hz were used. All potentials are referenced to decamethylferrocene; $E_{1/2}$ for sublimed ferrocene was 0.55 V.

Preparation of (11-Phthalimidoundecyl)ferrocene and (11-Aminoundecyl)ferrocene. $Fc(CH_2)_{11}Br$ (1.56 g, 3.7 mmol) was heated with potassium phthalimide (0.65 g, 3.5 mmol) in DMSO (25 mL) for 3 h at 120 °C. The organic layer was extracted into CH_2Cl_2 and washed several times with water to remove DMSO. Column chromatography (SiO_2, CH_2Cl_2) yielded (ferrocenylundecyl)phthalimide as a yellow oil (1.66 g, 92%). Anal. Calcd for $C_{29}H_{35}FeNO_2$: C, 71.75; H, 7.27; N, 2.89. Found: C, 72.04; H, 7.45; N, 2.63. EI-MS: *m*/*e* 485 (M^+). ^1H NMR (δ, ppm): 1.2−1.7 (m, 18H, $-CH_2-$), 2.30 (m, 2H, $FcCH_2-$), 3.68 (t ($J = 7$ Hz), 2H, NCH_2-), 4.05 (m, 4H, Fc *H*), 4.10 (s, 5H, $-C_5H_5$), 7.70 (m, 2H, phenyl *H*), 7.84 (m, 2H, phenyl *H*).

Conversion to the amine was achieved by stirring the phthalimide in EtOH (50 mL) with hydrazine hydrate (12 mL) for 16 h. Solvent was removed under vacuum, and the resulting product was then heated at 80 °C with 10% HCl (100 mL) for 15 min. Diethyl ether was added to the cooled solution, and the amine was released by treatment with NaOH. Subsequent ether extraction yielded (11-aminoundecyl)ferrocene 0.67 g (55%).

Preparation of *N*-(CHR)$_x$-Ferrocenyl Derivatives from Naphthalic Anhydrides. A typical preparation, that of **1b**, follows. $FcCH_2NH_2$ (0.215 g, 1 mmol) and 1,8-naphthalic anhydride (0.20 g, 1 mmol) in absolute alcohol (15 mL) were heated under reflux for 30 min, during which time an orange precipitate formed. This was filtered and recrystallized from CH_2Cl_2 layered with hexane to give orange crystals of **1b**. The filtrate was evaporated and the residue purified by column chromatography (SiO_2, CH_2Cl_2) to give a combined yield of 0.20 g (51%).

Anal. Calcd for $C_{23}H_{17}FeNO_2$: C, 69.90; H, 4.34; N, 3.54. Found: C, 69.63; H, 4.41; N, 3.75. EI-MS: *m*/*e* 395 (M^+). ^1H NMR (δ, ppm): 4.08, 4.51 (2 × (t, 2H, Fc *H*)), 4.26 (s, 5H, $-C_5H_5$), 5.14 (s, 2H, $-CH_2-$), 7.72 (dd ($J = 8.3$, 7.3 Hz), 2H, naphth β-*H*), 8.16 (dd ($J = 8.3$, 1.1 Hz), 2H, naphth γ-*H*), 8.58 (dd ($J = 7.3$, 1.1 Hz), 2H, naphth α-*H*). IR (CH_2Cl_2): ν_{CO} 1699, 1659 cm^{-1}.

1a: from 1,8-naphthalic anhydride/$FcNH_2$; red crystals 6%. For characterization, see below.

1c: from 1,8-naphthalic anhydride/$FcCH(Me)NH_2$; orange crystals 28%. Anal. Calcd for $C_{24}H_{19}FeNO_2$: C, 70.44; H, 4.68; N, 3.42. Found: C, 70.14; H, 4.53; N, 3.52. EI-MS: *m*/*e* 409 (M^+). ^1H NMR (δ, ppm): 1.96 (d ($J = 7.1$ Hz), 3H, methyl *H*), 4.08, 4.16, 4.24, 4.63 (4 × (m, 1H, Fc *H*)), 4.19 (s, 5H, $-C_5H_5$), 6.38 (q ($J = 7.1$ Hz), $-CHMe-$), 7.70 (dd ($J = 8.3$, 7.3 Hz), 2H, naphth β-*H*), 8.15 (dd ($J = 8.3$, 1.1 Hz), 2H, naphth γ-*H*), 8.52 (br, 2H, naphth α-*H*). IR (CH_2Cl_2): ν_{CO} 1700, 1660 cm^{-1}.

1d: from 1,8-naphthalic anhydride/$Fc(CH_2)_{11}NH_2$; 57% as a yellow oil. Anal. Calcd for $C_{33}H_{37}FeNO_2$: C, 74.02; H, 6.96; N, 2.62. Found: C, 74.02; H, 6.96; N, 2.65. EI-MS: *m*/*e* 535 (M^+).

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^{1}H NMR (δ, ppm): 1.2−1.5 (m, 16H, $-CH_2-$), 1.73 (m, 2H, NCH_2CH_2-), 2.30 (t (J = 7.8 Hz), 2H, $FcCH_2-$), 4.01, 4.04 (2 × (t, 2H, Fc *H*)), 4.07 (s, 5H, $-C_5H_5$), 4.16 (m, 2H, NCH_2-), 7.70 (dd (J = 8.3, 7.2 Hz), 2H, naphth *β-H*), 8.15 (dd (J = 8.3, 1.2 Hz), 2H, naphth *γ-H*), 8.55 (dd (J = 7.2, 1.2 Hz), 2H, naphth α-*H*). IR (CH_2Cl_2): ν_{CO} 1700, 1660 cm^{-1}.

2b: from 4-bromo-1,8-naphthalic anhydride/$FcCH_2NH_2$; orange crystals 41%. Anal. Calcd for $C_{23}H_{16}BrFeNO_2$: C, 58.27; H, 3.40; N, 2.95. Found: C, 58.21; H, 3.64; N, 3.02. Electrospray-MS: *m*/*e* 473 (M$^+$). ^{1}H NMR (δ, ppm): 4.08, 4.50 (2 × (t, 2H, Fc *H*)), 4.22 (s, 5H, $-C_5H_5$), 5.12 (s, 2H, $-CH_2-$), 7.81 (dd (J = 8.6, 7.2 Hz), naphth *H6*), 8.01 (d (J = 8 Hz), naphth *H3*), 8.39 (d (J = 8 Hz), naphth *H2*), 8.53 (dd (J = 8.6, 1.1 Hz), naphth *H5*), 8.63 (dd (J = 7.2, 1.1 Hz), naphth *H7*). IR (CH_2Cl_2): ν_{CO} 1702, 1664 cm^{-1}.

2d: from 4-bromo-1,8-naphthalic anhydride/$Fc(CH_2)_{11}NH_2$; orange oil, 75%. Anal. Calcd for $C_{33}H_{36}BrFeNO_2$: C, 64.51; H, 5.91; N, 2.28. Found: C, 64.20; H, 6.05; N, 2.19. Electrospray-MS: *m*/*e* 613 (M$^+$). ^{1}H NMR (δ, ppm): 1.2−1.5 (m, 16H, $-CH_2-$), 1.73 (m, 2H, NCH_2CH_2-), 2.30 (t (J = 7.7 Hz), 2H, $FcCH_2-$), 4.0 (m, 4H, Fc *H*), 4.08 (s, 5H, $-C_5H_5$), 4.16 (m, 2H, NCH_2-), 7.83 (dd (J = 8.5, 7.3 Hz), naphth *H6*), 8.03 (d (J = 7.9 Hz), naphth *H3*), 8.41 (d (J = 7.9 Hz), naphth *H2*), 8.56 (dd (J = 8.5, 1.1 Hz), naphth *H5*), 8.65 (dd (J = 7.3, 1.1 Hz), naphth *H7*). IR (neat oil): ν_{CO} 1703, 1663 cm^{-1}.

3b: from 3-nitro-1,8-naphthalic anhydride/$FcCH_2NH_2$; dark red crystals, 29%. Anal. Calcd for $C_{23}H_{16}FeN_2O_4$: C, 62.75; H, 3.66; N, 6.36. Found: C, 62.66; H, 3.40; N, 6.58. EI-MS: *m*/*e* 440 (M$^+$). ^{1}H NMR (δ, ppm): 4.10, 4.50 (2 × (t, 2H, Fc *H*)), 4.23 (s, 5H, $-C_5H_5$), 5.16 (s, 2H, $-CH_2-$), 7.91 (dd (J = 8.4, 7.4 Hz), naphth *H6*), 8.38 (dd (J = 8.4, 1.2 Hz), naphth *H5*), 8.75 (dd (J = 7.4, 1.2 Hz), naphth *H7*), 9.09 (d (J = 2.2 Hz), naphth *H4*), 9.30 (d (J = 2.2 Hz), naphth *H2*). IR (CH_2Cl_2): ν_{CO} 1707, 1669 cm^{-1}.

3c: from 3-nitro-1,8-naphthalic anhydride/FcCH(Me)NH_2; brown crystals, 11%. Anal. Calcd for $C_{24}H_{18}FeN_2O_4$: C, 63.46; H, 3.99; N, 6.17. Found: C, 63.48; H, 3.88; N, 6.34. EI-MS: *m*/*e* 454 (M$^+$). ^{1}H NMR (δ, ppm): 1.97 (d (J = 7.1 Hz), 3H, methyl *H*), 4.11, 4.19, 4.22, 4.66 (4 × (m, 1H, Fc *H*)), 4.22 (s, 5H, $-C_5H_5$), 6.33 (q (J = 7.1 Hz), −C*H*Me−), 7.88 (dd (J = 8.4, 7.4 Hz), naphth *H6*), 8.37 (dd (J = 8.4, 1.1 Hz), naphth *H5*), 8.71 (br m, naphth *H7*), 9.08 (d (J = 2.2 Hz), naphth *H4*), 9.22 (br, naphth *H2*). IR (CH_2Cl_2): ν_{CO} 1707, 1668 cm^{-1}.

4b: from 4-nitro-1,8-naphthalic anhydride/$FcCH_2NH_2$; green crystals, 33%. Anal. Calcd for $C_{23}H_{16}FeN_2O_4$: C, 62.75; H, 3.66; N, 6.36. Found: C, 62.95; H, 3.51; N, 6.49. EI-MS: *m*/*e* 440 (M$^+$). ^{1}H NMR (δ, ppm): 4.10, 4.49 (2 × (t, 2H, Fc *H*)), 4.23 (s, 5H, $-C_5H_5$), 5.14 (s, 2H, $-CH_2-$), 7.95 (dd (J = 8.7, 7.3 Hz), naphth *H6*), 8.38 (d (J = 8.0 Hz), naphth *H3*), 8.67 (d (J = 8.0 Hz), naphth *H2*), 8.72 (dd (J = 7.3, 1.1 Hz), naphth *H7*), 9.30 (dd (J = 8.7, 1.1 Hz), naphth *H5*). IR (CH_2Cl_2): ν_{CO} 1707, 1667 cm^{-1}.

4c: from 4-nitro-1,8-naphthalic anhydride/FcCH(Me)NH_2; brown crystals, 3%. EI-MS for $C_{24}H_{18}FeN_2O_4$: *m*/*e* 454 (M$^+$). ^{1}H NMR (δ, ppm): 1.97 (d (J = 7.1 Hz), 3H, methyl *H*), 4.09, 4.17, 4.22, 4.62 (4 × (m, 1H, Fc *H*)), 4.20 (s, 5H, $-C_5H_5$), 6.34 (q (J = 7.1 Hz), −C*H*Me−), 7.94 (dd (J = 8.7, 7.4 Hz), naphth *H6*), 8.36 (d (J = 8.0 Hz), naphth *H3*), 8.7 (br m, naphth *H2* and *H7*), 8.80 (dd (J = 8.7, 1.1 Hz), naphth *H5*). IR (CH_2Cl_2): ν_{CO} 1707, 1664 cm^{-1}.

4d: from 4-nitro-1,8-naphthalic anhydride/$Fc(CH_2)_{11}NH_2$; yellow crystals, 63%. Anal. Calcd for $C_{33}H_{36}FeN_2O_4$: C, 68.28; H, 6.25; N, 4.83. Found: C, 68.31; H, 6.18; N, 4.80. Electrospray-MS: *m*/*e* 580 (M$^+$). ^{1}H NMR (δ, ppm): 1.2−1.5 (m, 16H, $-CH_2-$), 1.74 (m, 2H, NCH_2CH_2-), 2.30 (t (J = 7.7 Hz), 2H, $FcCH_2-$), 4.02, 4.05 (2 × (t, 2H, Fc *H*)) 4.08 (s, 5H, $-C_5H_5$), 4.18 (m, 2H, NCH_2-), 7.98 (dd (J = 8.7, 7.5 Hz), naphth *H6*), 8.40 (d (J = 8.1 Hz), naphth *H3*), 8.69 (d (J = 8.1 Hz), naphth *H2*), 8.74 (dd (J = 7.5, 1.2 Hz), naphth *H7*), 8.84 (dd (J = 8.7, 1.2 Hz), naphth *H5*). IR (CH_2Cl_2): ν_{CO} 1708, 1667 cm^{-1}.

4e: from 4-nitro-1,8-naphthalic anhydride/1′-bromoaminoferrocene; 8%. Anal. Calcd for $C_{22}H_{13}BrFeN_2O_4$: C, 52.31; H, 2.59; N, 5.55. Found: C, 52.60; H, 2.51; N, 5.41. EI-MS: *m*/*e* 504 (M$^+$). ^{1}H NMR (δ, ppm): 4.25, 4.37, 4.52, 4.89 (4 × (m, 2H, Fc *H*)), 8.02 (dd (J = 8.8, 7.4 Hz), naphth *H6*), 8.44 (d (J = 8.0 Hz), naphth *H3*), 8.74 (d (J = 8.0 Hz), naphth *H2*), 8.80 (dd (J = 7.3, 1.1 Hz), naphth *H7*), 8.87 (dd (J = 8.8, 1.1 Hz), naphth *H5*). IR (CH_2Cl_2): ν_{CO} 1719, 1682 cm^{-1}.

5b: from 1,4,5,8-naphthalic dianhydride/$FcCH_2NH_2$; green solid, 87%. Anal. Calcd for $C_{36}H_{26}Fe_2N_2O_4 \cdot H_2O$: C, 63.56; H, 4.15; N, 4.12. Found: C, 63.89; H, 3.82; N, 4.03. IR (KBr disk): ν_{CO} 1703, 1665 cm^{-1}.

5c: from 1,4,5,8-naphthalic dianhydride/FcCH(Me)NH_2; green solid, 2%. Anal. Calcd for $C_{38}H_{30}Fe_2N_2O_4$: C, 66.11; H, 4.38; N, 4.06. Found: C, 64.01; H, 4.35; N, 3.99. FAB-MS: *m*/*e* 690 (M$^+$). ^{1}H NMR (δ, ppm): 1.96 (d (J = 7.1 Hz), 6H, methyl *H*), 4.09, 4.17, 4.22, 4.63 (4 × (m, 2H, Fc *H*)), 4.19 (s, 10H, $-C_5H_5$), 6.33 (q (J = 7.1 Hz), 2H, −C*H*Me−), 8.63 (br, 4H, naphth *H*). IR (CH_2Cl_2): ν_{CO} 1704, 1665 cm^{-1}.

5d: from 1,4,5,8-naphthalic anhydride/$Fc(CH_2)_{11}NH_2$; yellow crystals, 73%. Anal. Calcd for $C_{56}H_{66}Fe_2N_2O_4$: C, 71.34; H, 7.06; N, 2.97. Found: C, 71.59; H, 7.05; N, 2.93. Electrospray-MS: *m*/*e* 942 (M$^+$). ^{1}H NMR (δ, ppm): 1.2−1.5 (m, 32H, $-CH_2-$), 1.7 (m, 4H, NCH_2CH_2-), 2.29 (t (J = 7.7 Hz), 4H, $FcCH_2-$), 4.03, 4.04 (2 × (m, 4H, Fc *H*)), 4.09 (s, 10H, $-C_5H_5$), 4.19 (m, 4H, NCH_2-), 8.75 (br, 4H, naphth *H*). IR (CH_2Cl_2): ν_{CO} 1705, 1666 cm^{-1}.

Preparation of 1d via a Gabriel Synthesis. $Fc(CH_2)_{11}Br$ (0.508 g, 1.2 mmol) was heated with potassium naphthalimide (0.285 g, 1.2 mmol) in DMSO (10 mL) for 2 h at 120 °C. The organic layer was extracted into CH_2Cl_2 and washed several times with water to remove DMSO. Column chromatography (SiO_2, CH_2Cl_2) gave **1d** as a yellow oil (0.47 g, 73%).

Preparation of *N*-Ferrocenyl Compounds from Naphthalimides. A typical preparation, that of **1a**, follows. FcBr (0.265 g, 1 mmol), 1,8-naphthalimide (0.237 g, 1.2 mmol), and Cu_2O (0.086 g, 0.6 mmol) in 4-picoline (5 mL) were heated under reflux for 24 h. H_2SO_4 (5%, 100 mL) was added, and the organic phase was extracted with CH_2Cl_2. After a further wash with 5% H_2SO_4, this fraction was dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was purified by column chromatography (SiO_2, CH_2Cl_2) and recrystallized from CH_2Cl_2 layered with hexane to give red crystals of **1a** (0.237 g, 62%). Anal. Calcd for $C_{22}H_{15}FeNO_2$: C, 69.32; H, 3.97; N, 3.67. Found: C, 69.53; H, 3.74; N, 3.65. EI-MS: *m*/*e* 381 (M$^+$). ^{1}H NMR (δ, ppm): 4.26 (s, 5H, $-C_5H_5$), 4.28, 4.76 (2 × (t, 2H, Fc *H*)), 7.78 (dd (J = 8.3, 7.3 Hz), 2H, naphth *β-H*), 8.23 (dd (J = 8.3, 1.1 Hz), 2H, naphth *γ-H*), 8.65 (dd (J = 7.3, 1.1 Hz), 2H, naphth α-*H*). IR (CH_2Cl_2): ν_{CO} 1712, 1674 cm^{-1}.

4a: from 4-nitro-1,8-naphthalimide/FcBr; green crystals, 2%. Anal. Calcd for $C_{22}H_{14}FeN_2O_4$: C, 62.00; H, 3.31; N, 6.57. Found: C, 61.95; H, 3.45; N, 6.53. EI-MS: *m*/*e* 426 (M$^+$). ^{1}H NMR (δ, ppm): 4.27 (s, 5H, $-C_5H_5$), 4.32, 4.74 (2 × (t, 2H, Fc *H*)), 8.01 (dd (J = 8.7, 7.3 Hz), naphth *H6*), 8.44 (d (J = 8.1 Hz), naphth *H3*), 8.74 (d (J = 8.1 Hz), naphth *H2*), 8.78 (dd (J = 7.3, 1.1 Hz), naphth *H7*), 8.87 (dd (J = 8.7, 1.1 Hz), naphth *H5*). IR (CH_2Cl_2): ν_{CO} 1719, 1680 cm^{-1}.

6a: from 2,3-naphthalenedicarboximide/FcBr; orange crystals, 71%. Anal. Calcd for $C_{22}H_{15}FeNO_2$: C, 69.32; H, 3.97; N, 3.67. Found: C, 69.06; H, 3.94; N, 3.79. EI-MS: *m*/*e* 381 (M$^+$). ^{1}H NMR (δ, ppm): 4.23 (s, 5H, $-C_5H_5$), 4.22, 5.10 (2 × (t, 2H, Fc *H*)), 7.71 (m, 2H, naphth *H6, H7*), 8.07 (m, 2H, naphth *H5, H8*), 8.37 (s, 2H, naphth *H1, H4*). IR (CH_2Cl_2): ν_{CO} 1770, 1713 cm^{-1}.

Preparation of 6b−d from 2,3-Naphthalenedicarboxylic Acid. A typical preparation, that of **6b**, follows. $FcCH_2NH_2$ (0.215 g, 1 mmol) and 2,3-naphthalenedicarboxylic acid (0.216 g, 1 mmol) were heated as a melt for 30 min. The residue was purified by column chromatography (SiO_2, CH_2Cl_2). Recrystallization from CH_2Cl_2 layered with hexane gave yellow crystals of **6b**; 0.130 g (33%). Anal. Calcd for $C_{23}H_{17}$-

$FeNO_2$: C, 69.90; H, 4.34; N, 3.54. Found: C, 69.60; H, 4.39; N, 3.63. EI-MS: *m*/*e* 395 (M^+). ^1H NMR (δ, ppm): 4.11, 4.40 (2 × (t, 2H, Fc *H*)), 4.20 (s, 5H, $-C_5H_5$), 4.67 (s, 2H, $-CH_2-$), 7.67 (m, 2H, naphth *H6*, *H7*), 8.03 (m, 2H, naphth *H5*, *H8*), 8.30 (s, 2H, naphth *H1*, *H4*). IR (CH_2Cl_2): ν_{CO} 1765, 1709 cm^{-1}.

6c: from 2,3-naphthalenedicarboxylic acid/FcCH(Me)NH_2; yellow crystals, 24%. Anal. Calcd for $C_{24}H_{19}FeNO_2$: C, 70.44; H, 4.68; N, 3.42. Found: C, 70.47; H, 4.77; N, 3.40. EI-MS: *m*/*e* 409 (M^+). ^1H NMR (δ, ppm): 1.91 (d (J = 7.2 Hz), 3H, methyl *H*), 4.10, 4.16, 4.24, 4.52 (4 × (m, 1H, Fc *H*)), 4.16 (s, 5H, $-C_5H_5$), 5.44 (q (J = 7.2 Hz), $-CH$Me$-$), 7.65 (m, 2H, naphth *H6*, *H7*), 8.01 (m, 2H, naphth *H5*, *H8*), 8.26 (s, 2H, naphth *H1*, *H4*). IR (CH_2Cl_2): ν_{CO} 1764, 1708 cm^{-1}.

6d: from 2,3-naphthalenedicarboxylic acid/Fc$(CH_2)_{11}NH_2$; yellow crystals, 61%. Anal. Calcd for $C_{33}H_{37}FeNO_2$: C, 74.02; H, 6.96; N, 2.62. Found: C, 73.95; H, 7.01; N, 2.57. EI-MS: *m*/*e* 535 (M^+). ^1H NMR (δ, ppm): 1.2–1.5 (m, 16H, $-CH_2-$), 1.70 (m, 2H, NCH_2CH_2-), 2.30 (t (J = 7.6 Hz), 2H, $FcCH_2-$), 3.74 (t (J = 7.3 Hz), 2H, NCH_2-), 4.03, 4.04 (2 × (t, 1H, Fc *H*)), 4.08 (s, 5H, $-C_5H_5$), 7.67 (m, 2H, naphth *H6*, *H7*), 8.03 (m, 2H, naphth *H5*, *H8*), 8.30 (s, 2H, naphth *H1*, *H4*). IR (CH_2Cl_2): ν_{CO} 1765, 1705 cm^{-1}.

Preparation of 7. 2b (0.113 g, 0.24 mmol) and ethynylferrocene (0.07 g, 0.33 mmol) were refluxed for 30 min in diisopropylamine with $Pd(PPh_3)_2Cl_2$ (5 mg) and CuI (1.3 mg). The residue was purified on preparative TLC plates (SiO_2) using CH_2Cl_2/hexane (2:1) eluent. Recrystallization from CH_2Cl_2 layered with hexane gave dark red crystals of **7**; 39 mg (27%). Anal. Calcd for $C_{35}H_{25}Fe_2NO_2$: C, 69.68; H, 4.18; N, 2.32. Found: C, 69.44; H, 4.23; N, 2.40. Electrospray-MS: *m*/*e* 603 (M^+). ^1H NMR (δ, ppm): 4.09, 4.52 (2 × (t, 2H, $-CH_2$Fc *H*)), 4.23 (s, 5H, $-CH_2$Fc C_5H_5), 4. 30 (s, 5H, $-C\equiv C$Fc C_5H_5), 4.37, 4.64 (2 × (t, 2H, $-C\equiv C$Fc *H*)), 5.13 (s, 2H, $-CH_2-$), 7.80 (dd (J = 8.7, 7.2 Hz), naphth *H6*), 7.86 (d (J = 8 Hz), naphth *H3*), 8.51 (d (J = 8 Hz), naphth *H2*), 8.6 (m, 2H, naphth *H5* & *H7*). IR (CH_2Cl_2): $\nu_{C\equiv C}$ 2202; ν_{CO} 1698, 1660 cm^{-1}.

X-ray Data Collection, Reduction, and Structure Solution for 3b. Crystal data for **3b** are given in Table 3. The compound was recrystallized from dichloromethane/hexane and a orange-red plate was used for data collection. Data were collected at 158(2) K on a Bruker SMART CCD diffractometer, processed using SMART[37a] and empirical absorption corrections applied using SADABS.[37b] The structure was solved using SHELXS-97[37c] and refined by full-matrix least squares on F^2 using SHELXL-97.[37d] All non-hydrogen atoms were assigned anisotropic temperature factors, with hydrogen atoms included in calculated positions. Final positional and equivalent thermal parameters for **3b** are given in the Supporting Information.

Table 3. Crystal Data and Structure Refinement Details for 3b

chem formula	$C_{23}H_{16}N_2O_4Fe$
fw	440.23
cryst syst	monoclinic
space group	$P2_1/c$
abs coeff	0.859 mm^{-1}
final R indices ($I > 2\sigma(I)$)	R1 = 0.0311, wR2 = 0.0624
R indices (all data)	R1 = 0.0505, wR2 = 0.0643
goodness of fit on F^2	0.996
unit cell dimens	
a	22.526(8) Å
b	8.981(3) Å
c	9.210(3) Å
β	100.56(4)°
V	1831.8(11) $Å^3$
Z	4
temp	158(2) K
density (calcd)	1.596 Mg/m^3
no. of rflns collected	22613
no. of indep rflns	3683 (R(int) = 0.0486)

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Supporting Information Available: Tables of X-ray crystallographic data for **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000352E

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[37] (a) SMART CCD software; Bruker AXS, Madison, WI, 1994. (b) SADABS; Bruker AXS, Madison, WI, 1997. (c) Sheldrick, G. M. SHELXS-97; University of Göttingen, Göttingen, Germany, 1990. (d) Sheldrick, G. M. SHELXL-97; University of Göttingen, Göttingen, Germany, 1997.