

NOVEL FLUORESCENT
ORGANOMETALLIC MATERIALS

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ABSTRACT

This thesis describes the synthesis and properties of some extended donor-acceptor dyads with the donor being a ferrocenyl moiety and a fluorescent naphthalimide group as the acceptor. Two series of extended ferrocenyl-naphthalimide dyads were prepared in reasonable yield depending on the synthetic route. The first are a series of three ferrocenyl-CH=CH-spacer-C≡C-naphthalimide dyads in which the spacers are phenyl, biphenyl and anthryl and the second are a series of three ferrocenyl-C≡C-spacer-C≡C-naphthalimide dyads in which the spacers are 2,2'-bithiophene, 2,5-dimethoxybenzene and tetrafluorobenzene groups.

The molecular structures of some compounds have been determined by X-ray diffraction although with many challenges because of the extensive π - π stacking of molecules that leads to ready aggregation in the solid state, particularly for the ferrocenyl-CH=CH-spacer-C≡C-naphthalimide dyads, in which the naphthalimide bears a methyl head group. In order to reduce the π - π stacking effect between the molecules and also to produce chiral molecules for the potential nonlinear optical applications, a chiral α -methylbenzylamine was introduced as the head group of naphthalimide for the ferrocenyl-C≡C-spacer-C≡C-naphthalimide dyads. The resulting compounds successfully gave crystals of sufficient quality for X-ray structural investigation.

While the oxidative electrochemistry of the ferrocenyl compound in the two series of dyads was largely predictable ($E^\circ \sim 0.55$ V for ferrocenyl-CH=CH- and ~ 0.72 V for ferrocenyl-C≡C-), the presence of spacers in the dyads appeared to afford stability to the reduced naphthalimide species. This was exhibited by the appearance of chemically reversible one-electron reduction processes for each of the compounds investigated. Similar unusual chemical reversibility was also shown by the spacer-C≡C-naphthalimide precursor systems. For the ferrocenyl-CH=CH-spacer-C≡C-naphthalimide dyads, the oxidation and reduction potentials closely resembled those of the simple ferrocenyl-CH=CH-spacer systems. This suggested that augmentation of the simple ferrocenyl-CH=CH-phenyl, -biphenyl and -anthryl systems with an alkyne linked naphthalimide unit showed little influence on the oxidation of the ferrocenyl moiety or the reduction of the naphthalimide unit. However, for

the ferrocenyl-C≡C-spacer-C≡C-naphthalimide dyads, the oxidation and reduction potentials are influenced by the inductive effects of the spacers. While an anodic shift was observed for the dyad with the electron-withdrawing spacer tetrafluorobenzene, a cathodic shift was displayed for the dyads with the electron-donating spacers 2,2'-bithiophene and 2,5-dimethoxybenzene compared to that in the simple ferrocenyl-C≡C-naphthalimide system.

The spectroscopic properties of the ferrocenyl-CH=CH-spacer-C≡C-naphthalimide dyads showed that interpolation of the aromatic spacers does not interfere with the internal charge separation. Oxidation of the ferrocenyl moiety resulted in bleaching of the metal-to-ligand charge transfer band at ~ 500 nm and the growth of a new band in the near infrared region at ~ 1000 nm. This new band can be assigned to a ligand-to-metal charge transfer transition, where the ferrocenium now acts as an acceptor to the naphthalimide donor.

For the ferrocenyl-C≡C-spacer-C≡C-naphthalimide dyads, the spectroscopic properties showed that the mutually electron-withdrawing tetrafluorobenzene and naphthalimide units had little interaction despite their connection by a conductive alkyne link. In contrast, the dyads containing the electron-donating 2,2'-bithiophene and 2,5-dimethoxybenzene showed some degree of interaction between the spacer and the naphthalimide fragments. This was evidenced by the appearance of a broad absorption band in the range 410 - 440 nm, which is associated with an orbital that is delocalised between the spacer and the naphthalimide fragments. Again, the roles of donor and acceptor were reversed on oxidation of the ferrocenyl moiety. This resulted in the growth of a new near infrared band at ~750 nm for the dyad containing the tetrafluorobenzene spacer and at ~ 1000 nm for the dyads with 2,2'-bithiophene and 2,5-dimethoxybenzene spacers. The ferrocenyl unit went from being a net donor to ferrocenium, which was acting as an acceptor, with the tetrafluorobenzene spacer adopting the donor role more reluctantly than the delocalised 2,2'-bithiophene-C≡C-naphthalimide and 2,5-dimethoxybenzene-C≡C-naphthalimide moieties.

1,3,5-Tri- and 1,2,4,5-tetra-substituted benzene cores were also used as spacers for the preparation of extended arrays of ferrocenyl-naphthalimide dyads. Utilisation of the 1,3,5-tri-substituted benzene core enabled the core to be embellished in three directions, resulting in Y-motif extended arrays containing either one ferrocenyl unit [(ethenylferrocenyl)-C₆H₃-(C≡C-C₆H₅)₂] or one naphthalimide moiety [(4-piperidino-*N*-propargyl-naphthalimide)-C₆H₃-(Br)₂]. With the 1,2,4,5-tetra-substituted benzene core, the extension of the core was possible in four directions and gave extended arrays in an X-motif. Again, these systems contained either ferrocenyl units [bis(alkoxyferrocenyl)-C₆H₂-(C≡C-C₆H₅)₂] or naphthalimide moieties [(tetrakis-naphthalimide)-C₆H₂]. Attempts to incorporate both ferrocenyl and naphthalimide fragments into the X- or Y-motif extended arrays were unsuccessful.

By adding C₂Co₂(CO)₆dppm across the triple bonds of two of the four alkyne groups in the X-motif naphthalimide system [(tetrakis-naphthalimide)-C₆H₂], it was possible to incorporate two oxidisable C₂Co₂(CO)₄dppm cluster units into the molecule. The electrochemistry of the resulting system showed two discrete oxidation processes, suggesting the possibility of some interaction between the dicobalt cluster redox centres.

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