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Novel U-Shaped Systems Containing an Imide-Functionalized Cleft for the Study of Solvent-Mediated Electron Transfer and Energy Transfer: Synthesis and Binding Studies[**]

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One of the most intensively investigated issues of long-range electron transfer (ET) and energy transfer (EnT) is how the electronic coupling for these processes depends on the nature of the intervening medium between a pair of chromophores.[1] Using structurally well-defined systems, considerable progress has been made in delineating the characteristics of electronic coupling involving saturated hydrocarbon bridges,[1a–c] protein-like pathways,[1d] and the π stacks of base pairs in DNA molecules.[1e]

By contrast, solvent-mediated electronic coupling remains a vexing issue, owing to the dynamic, jostling nature of the solvent molecules which blur the electronic coupling pathways. Progress has recently been made by using novel rigid U-shaped multichromophoric systems, represented by Class I in Figure 1,[2] in which the terminal chromophores face each other across a "rigid" cavity within which a certain number of solvent molecules are present (in a dynamic sense). However, because these systems still do not address the problem of

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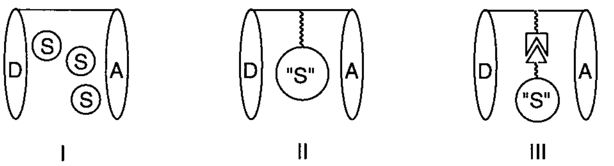


Figure 1. Modes of solvent inclusion within a U-shaped cavity. Class I: Unconstrained solvent; Class II: Covalently attached; Class III: Noncovalently bound. D: Donor, A: Acceptor, S: Solvent.

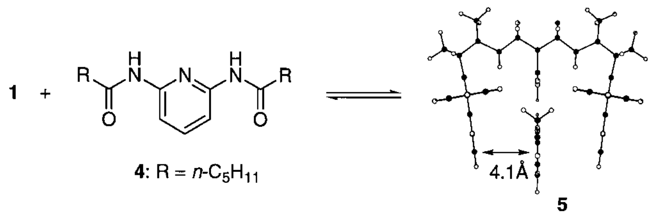


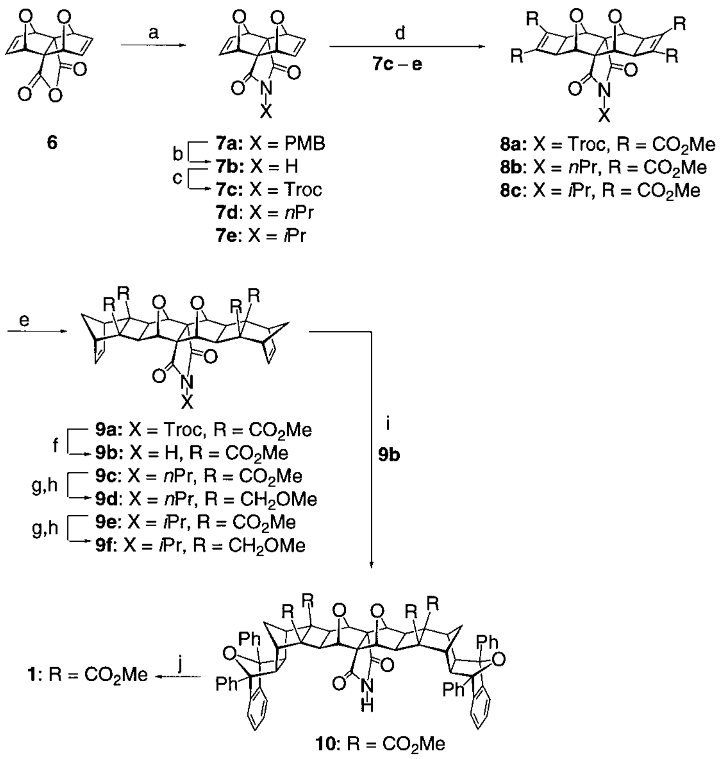
Figure 3. AM1-optimized structure for the H-bonded complex **5**.

solvent mobility, both the number of solvent molecules occupying the molecular cavity and the electronic coupling pathways remain ill-defined. This problem may be ameliorated by "freezing" the solvent molecule within the cavity, either by covalent attachment (Class II), or by noncovalent recognition forces, such as H-bonding (Class III).

We describe herein the synthesis of three representative members of a novel cavity-functionalized U-shaped system, **1**–**3** (Figure 2; see Table 1 for melting points and NMR data), which offer the exciting potential for acting as Class II and Class III systems in solvent-mediated ET and EnT studies. The key attribute of these molecules is the presence of the imide functionality within the cavity. Class II models are realized by covalent attachment of the "solvent" molecule to the imide nitrogen atom, in which case it has, at the most, only one rotational degree of freedom. Three-point H-bonding of a guest molecule to the imide functionality results in a Class III system in which all rotational degrees of freedom are frozen.

The AM1-optimized geometries of **1**–**3** (Figure 2) and the H-bonded complex, **5**, between **1** and 2,6-bis(hexanoylamino)pyridine **4** (Figure 3) are revealing. The interchromophore separation in these systems ranges between 7 and 10.5 Å, and the chromophores are proximal to the intervening "solvent" molecules, thereby ensuring reasonably strong chromophore–solvent electronic coupling.

The synthesis of **1** is summarized in Scheme 1, the key to which proved to be the correct selection of a protecting group for the imide functionality that would impart both suitable solubility to the system during the synthesis and ease of removal when the free imide group was required. Precedent[3] suggested the use of the p-methoxybenzyl (PMB) protecting group which may be removed using cerium(IV) ammonium nitrate (CAN).[4] Anhydride **6**[5] was treated with p-methoxybenzylamine to afford the corresponding amic-acid which was cyclized to give the imide **7a** in 42% yield. Although treatment of **7a** with CAN resulted in ready removal of the PMB group, to give **7b**, oxidative removal of this group at latter stages of the synthesis was problematical. The more readily removable trichloroethoxycarbamoyl (Troc) group[6] was therefore used and was introduced by NH deprotonation of **7b**, followed by quenching with 2,2,2-trichloroethylchloroformate, to give **7c**. The imide **7c** was converted into the tetraester **8a** by ruthenium-catalyzed [2+2] cycloaddition with dimethyl acetylenedicarboxylate (DMAD)[7] and then into the diene **9a** by Diels–Alder addition with cyclopentadiene.[8] The Troc group was cleanly removed in essentially quantitative yield upon treatment with zinc to give the bridge system **9b**.[6]



Scheme 1. a) 1. XNH$_2$ (X = p-MeOC$_6$H$_4$CH$_2$ (PMB), nPr, iPr), 2. NaOAc, Ac$_2$O; b) CAN; c) NaH, DMF, CCl$_3$CH$_2$O$_2$CCl; d) DMAD, [RuH$_2$CO(PPh$_3$)$_3$]; e) C$_5$H$_6$; f) Zn, dioxane, AcOH; g) LiAlH$_4$; h) 1. NaH, 2. MeI; i) DPIBF, dioxane, 120°C; j) TFA, C$_6$H$_6$.

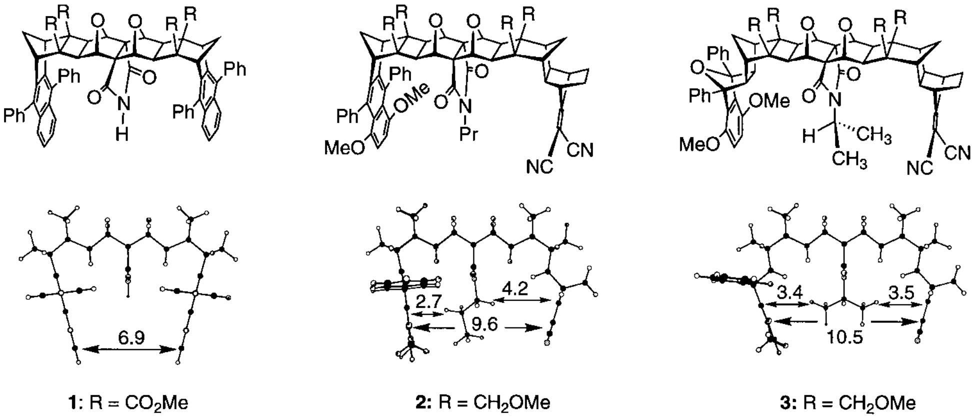


Figure 2. AM1-optimized structures for **1**–**3**. Distances in Å.

The system **9b** possesses two terminal norbornene double bonds to which a number of useful chromophores may be attached.[1b, 9] For our initial studies we elected to attach simple diphenylnaphthalene groups and this was readily accomplished by Diels–Alder addition of 1,3-diphenylisobenzofuran (DPIBF) to the double bonds[5b] of **9b** at 120 °C, followed by acid-catalyzed dehydration of the oxo-bridged bisadduct **10** to give **1**.

The binding abilities of the free imide systems **1**, **9b**, and **10** were assessed by determining their association constants K_a with the guest molecule **4**, from the complexation-induced ^{1}H NMR shifts of the imide proton (in $CDCl_3$). The K_a values for **1**, **9b**, and **10** are 946, 121, and 119 M^{-1}, respectively. The association constant for **1** is significantly larger than that typically reported for complexation between 2,6-bis(acylamino)pyridines with succinimides ($K_a = 50–500\,M^{-1}$),[10] and is most likely due to enhanced stabilization of the complex by π-stacking interactions between the guest molecule and the proximal naphthalene groups.

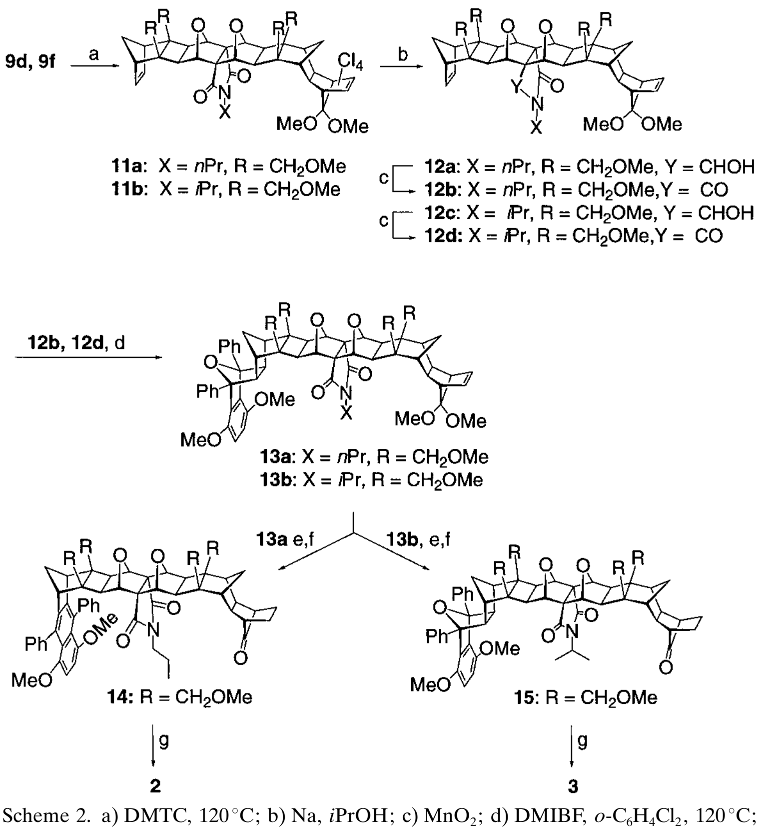
Scheme 2 illustrates how the synthesis may be extended to systems possessing different cavity sizes and having chromophores suitable for ET studies. In these systems, *n*-propyl and isopropyl "solvent" molecules have been covalently linked to the imide group.

The bridge ester groups of **9c** and **9e** (Scheme 1) were converted into the less chemically reactive methoxyethers **9d** and **9f**, respectively.[8] Diels–Alder reaction of dimethoxytetrachlorocyclopentadiene (DMTC)[11] with **9d** and **9f** gave the respective monoadducts **11a** and **11b**, together with unconverted starting material and some of the bisadducts. Reductive dechlorination of **11a** and **11b** (Na, *i*PrOH)[11] was accompanied by reduction of the imide groups to give the hydroxylactams **12a** and **12c**, respectively, oxidation of which gave the imides **12b** and **12d** in greater than 90% yield for both steps.

Diels–Alder addition of 4,7-dimethoxy-1,3-diphenylisobenzofuran (DMIBF)[12] to **12b** and **12d** slowly gave the respective adducts **13a** and **13b**. The naphthalene–ketone **14** was obtained from **13a** by catalytic hydrogenation, followed by trifluoroacetic acid (TFA) catalyzed simultaneous dehydration and deacetalization. In contrast, hydrogenation of **13b**, followed by TFA treatment, gave only deacetalized material **15**, without causing dehydration to form the naphthalene ring. Failure to effect aromatization in this system is due to the increased degree of steric congestion within the molecular cavity caused by the bulky *i*Pr group. Knoevenagel condensation of the ketones **14** and **15** with malononitrile afforded **2** and **3**, respectively.[11]

Cyclic voltammetry and UV spectroscopy of suitable model compounds indicate that both the diphenyldimethoxynaphthalene and dimethoxybenzene groups should be suitable donor chromophores for effecting photoinduced ET to the dicyanovinyl (DCV) acceptor.[13] Indeed, preliminary steady-state fluorescence studies on **2** and **3** in acetonitrile revealed quenching of the naphthalene fluorescence, to the extent of 92% and 49%, respectively. [14] These results strongly indicate that photoinduced ET is occurring in these systems and that it is particularly efficient in **2**.

In summary, we have demonstrated a viable synthetic route to novel U-shaped systems of the type **1**–**3** which offer considerable scope in exploring a variety of neighboring group interactions under structurally well-defined conditions. In particular, their deployment in photophysical investigations should provide valuable insight into the mechanism of solvent-mediated ET and EnT processes. Efforts are currently being directed towards synthesizing a range of systems, based on architectural principles described above, which contain covalently linked "solvent" groups, particularly aromatic units.



Scheme 2. a) DMTC, 120 °C; b) Na, *i*PrOH; c) MnO_2; d) DMIBF, *o*-$C_6H_4Cl_2$, 120 °C; e) H_2, Pd/C; f) TFA, C_6H_6; g) $CH_2(CN)_2$, NH_4OAc, AcOH.

Table 1. Melting point and NMR data for **1**–**3**.

1: M.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.84$ (s, 4H), 2.05 (d, $J = 10.2$ Hz, 2H), 2.38 (d, $J = 10.2$ Hz, 2H), 3.59 (s, 16H), 5.08 (s, 4H), 7.16 (d, $J = 7.5$ Hz, 4H), 7.27–7.35 (m, 8H), 7.42–7.53 (m, 8H), 7.54–7.64 (m, 8H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 45.7$, 49.3, 51.9, 52.4, 58.1, 70.9, 81.3, 125.2, 126.7, 127.5, 128.5, 128.8, 129.9, 130.1, 131.5, 134.0, 137.2, 141.0, 171.1, 173.8.

2: M.p. > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.72$ (t, $J = 7.3$ Hz, 3H), 0.98–1.18 (m, 2H), 1.21–1.29 (m, 2H), 1.62 (s, 2H), 1.62–1.68 (m, 2H), 1.79 (d, $J = 9.7$ Hz, 1H), 1.88 (d, $J = 12.2$ Hz, 1H), 1.92–1.99 (m, 2H), 1.99–2.04 (m, 2H), 2.20 (s, 2H), 2.28 (s, 2H), 2.37 (s, 2H), 2.80 (d, $J = 8.9$ Hz, 2H), 2.97 (s, 2H), 3.00 (d, $J = 9.3$ Hz, 2H), 3.13 (s, 6H), 3.23 (s, 2H), 3.23 (s, 6H), 3.35 (s, 6H), 3.63 (d, $J = 8.9$ Hz, 2H), 3.65 (d, $J = 9.3$ Hz, 2H), 4.75 (s, 2H), 4.78 (s, 2H), 6.74 (s, 2H), 7.17 (t, $J = 8.0$ Hz, 4H), 7.27 (t, $J = 7.4$ Hz, 2H), 7.33 (t, $J = 7.4$ Hz, 2H), 7.41 (t, $J = 7.4$ Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 11.3$, 20.4, 21.6, 24.4, 33.5, 38.6, 38.7, 40.0, 44.2, 44.8, 45.4, 45.5, 50.2, 51.1, 52.8, 57.0, 58.7, 58.9, 69.5, 69.8, 70.7, 73.3, 81.3, 108.3, 110.9, 124.8, 125.3, 126.6, 127.1, 128.3, 128.4, 131.3, 142.7, 144.1, 151.9, 173.7, 191.9.

3: M.p. $>300\,^{\circ}$C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.57$ (d, $J = 10.6$ Hz, 1H), 0.98 (d, $J = 6.8$ Hz, 6H), 1.30 (d, $J = 12.0$ Hz, 1H), 1.68 (d, $J = 8.7$ Hz, 2H), 1.93 (d, $J = 12.0$ Hz, 1H), 2.00 (d, $J = 8.7$ Hz, 2H), 2.19 (d, $J = 10.6$ Hz, 1H), 2.34 (s, 2H), 2.39 (s, 2H), 2.44 (s, 2H), 2.46 (s, 2H), 2.47 (s, 2H), 2.60 (d, $J = 9.0$ Hz, 2H), 2.79 (s, 2H), 2.87 (d, $J = 9.0$ Hz, 2H), 3.04 (s, 2H), 3.16 (s, 6H), 3.29 (s, 6H), 3.33 (s, 6H), 3.59 (d, $J = 9.0$ Hz, 2H), 3.68 (d, $J = 9.0$ Hz, 2H), 4.10 (sept, $J = 6.8$ Hz, 1H), 4.79 (s, 2H), 4.83 (s, 2H), 6.53 (s, 2H), 7.33 (t, $J = 7.1$ Hz, 2H), 7.43 (t, $J = 7.1$ Hz, 4H), 7.80 (d, $J = 7.1$ Hz, 4H); ^{13}C NMR (75.5 MHz, CDCl$_3$): $\delta = 0.93$, 17.79, 21.69, 31.36, 33.51, 38.60, 40.10, 40.26, 43.31, 44.57, 44.82, 45.44, 48.92, 51.00, 52.94, 56.46, 58.69, 58.88, 69.57, 70.29, 73.66, 81.63, 81.91, 90.32, 110.93, 113.21, 126.89, 127.09, 128.23, 137.11, 138.36, 147.15, 173.84, 191.59.

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[13] Diphenyldimethoxynaphthalene: $E_{\mathrm{ox}}(\mathrm{CH_2Cl_2}) = 0.99$ eV, $E_{00} = 3.4$ eV. Dimethoxybenzene: $E_{\mathrm{ox}}(\mathrm{CH_3CN}) = 1.33$ eV, $E_{00} = 3.95$ eV. DCV: $E_{\mathrm{red}}(\mathrm{CH_3CN}) = -1.7$ eV. From these data, the driving forces for photoinduced ET from locally excited aromatic donor to DCV acceptor in **2** and **3** are estimated to be 0.8 and 0.9 eV, respectively.

[14] The fluorescence quantum yields for **2** and **3** were obtained relative to appropriate model systems lacking the DCV acceptor group.

Ruthenium-Catalyzed Intermolecular Hydroamination of Terminal Alkynes with Anilines: A Practical Synthesis of Aromatic Ketimines[**]

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Aromatic ketimines are an important class of compounds widely used for the preparation of a variety of nitrogen-containing chemicals, such as tertiary[1a] or secondary amines,[1b–d] nitrogen heterocycles,[1e, 2e,g] carboxylic amides,[1f, 2f] β-enamino esters,[1g] amino alcohols,[1h] α-sulfinyl ketimines,[1i] and many others.[1j–l] Although the condensation of ketones with primary amines is a textbook route to ketimines, the procedure is sometimes not practical for the synthesis of *aromatic* ketimines because aromatic ketones react much more slowly than aliphtic ketones or aldehydes, and methyl ketones are sensitive to aldol-type side reactions.[2a] Therefore synthesis of imines from acetophenone often gives unsatisfactory results (for example, 40–55 % maximum yields from reactions with aniline[2b,d–f, 3]). Another practical route to aromatic ketimines is therefore desired to supplement the classical ketone–amine condensation pathway.

We thought that the hydroamination of phenylacetylene and its derivatives should be a convenient way to synthesize the compounds, and it deserved special attention in terms of its efficiency of atom utilization since it avoids the formation of stoichiometric amounts of by-products.[4] Compared to *intra*molecular cyclizations,[5] however, the *inter*molecular hydroaminations of alkynes[6] is more difficult, and only a few approaches exist.[4] Besides the established stoichiometric aminomercuration/reduction method,[7] the only catalytic reactions known are those with mercury or thallium,[6a,b] and metallocenes of zirconium,[6c] lanthanide,[6d,f] and actinide.[6e] These catalysts or precursors, though interesting in their own right, have problems associated with environmental protection, low activity, and/or air and moisture sensitivity.

Herein we disclose an efficient synthesis of aromatic ketimines based on the regioselective hydroamination of terminal alkynes with anilines using a ruthenium carbonyl catalyst. The incorporation of late transition metals in catalysts have an advantage over early transition metals, lanthanide, and actinide metals in that their low oxophilicity permits the use of many substrates for catalysis that are excluded in the systems with highly oxophilic metals. Yet, to the best of our knowledge, *inter*molecular hydroamination of alkynes by late transition metals other than mercury has not appeared in the literature. This situation is probably because of their very low activity (and small turnover numbers

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