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Photoinduced Electron and Energy Transfer in Aryldihydropyridines

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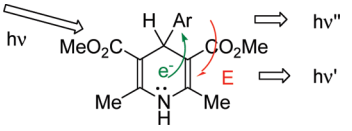

Dimethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylates (Hantzsch DHPs) fluoresce weakly in fluid solution. However, these compounds exhibit an efficient fluorescence both in a viscous medium (glycerin) at room temperature and in a glassy matrix at 77 K (but no phosphorescence, since ISC is negligible). DHPs bearing an aryl group in position 4 have been synthesized. These contain two different π systems separated by an sp^3 carbon (DHP-Ar dyads). The occurrence of energy and electron transfer processes between the chromophores is investigated through luminescence measurements. In particular, when ^{3}Ar emits at a slow rate (e.g., Ar = phenanthryl) or not at all (Ar = nitrophenyl) the intradyad forward/backward electron transfer sequence offers a path for arriving at the DHP-localized triplet and the corresponding phosphorescence is observed. When ^{3}Ar emits at a faster rate (Ar = acylphenyl), the phosphorescence from either of the two localized triplets, ^{3}Ar or ^{3}DHP, can be observed depending on λ_{exc}. When the aryl group has a triplet energy lower than that of ^{3}DHP, this functions as emitting (4-cyano-1-naphthyl) or nonemitting ($MeO_2CCH{=}CHC_6H_4$) energy sink. The results document the possibility of building tailor-made Hantzsch aryldihydropyridines as versatile photoactivated dyads.

Introduction

Supramolecular assemblies of increasing sophistication have been developed over the last decades, in most cases based on the use of transition metal ions, and demonstrated to be useful for a variety of light-induced applications, from molecular machines to systems that mimic chlorophyll photosynthesis.[1] However, simple organic dyads containing two separated chromophores may likewise be useful in this respect and have the advantage of possessing a strong scaffold of covalent bonds that can be varied almost at will in order to fit the desired properties by the synthetic methods of organic chemistry.[2] We recently pointed out a simple system that seems to incorporate a number of potentially useful characteristics, that of 4-aryl-1,4-dihydropyridines.[3] Dyads of this structure have been only sparsely investigated up to now. A few photochemical applications have been demonstrated, e.g., for photosensitive polymers,[4] and more can be envisaged, such as the use of dihydropyridines of appropriate structure as biosensors

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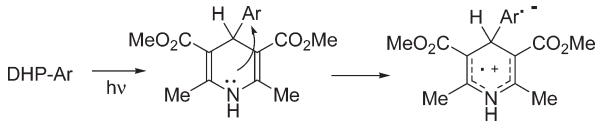
SCHEME 1



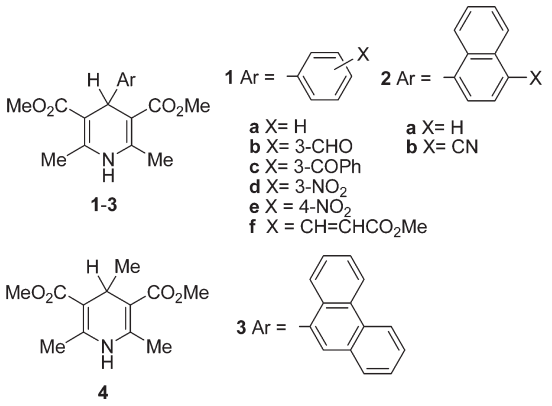
or for the mapping of enzyme kinetics by fluorescence similarly to NADH.[5]

A convenient basis structure is that of 1,4-dihydropyridine-3,5-dicarboxylates that are available through the versatile Hantzsch synthesis.[6] One can imagine that the ester functions can be elaborated in order to obtain molecules of different chemical characteristics, solubility, and ability to form complexes. Independently from this, the light-activated moiety can be freely elaborated by choosing the aldehyde in the Hantzsch synthesis. In particular, the dihydropyridine moiety may be exploited for an intramolecular electron transfer process by introducing a (substituted) aryl group in position 4 that functions as a reducible moiety (see Scheme 1).[7]

The dihydropyridine (DHP) chromophore (here and in the following reference is always to Hantzsch dihydropyridines, containing an enaminocarboxylate chromophore) is endowed by a strongly allowed absorption with the maximum around 350 nm and extending to the border of the visible. Thus, all of the UV is absorbed and when an appropriate electron-accepting substituent is present in position 4, intramolecular electron transfer can be quantitative and convert light into charge separation over a ca. 6 Å distance. Indeed, an example was previously found for the case of 4-(3-nitrophenyl)-1,4-dihydropyridine and some related compounds.[3] It was observed that in the parent 4-phenyl derivative (Ph-DHP) there was no interaction between the two moieties, as demonstrated by the fact that the weak fluorescence of this compound was identical to that of 4-unsubstituted DHP and was thus attributed to the unperturbed localized singlet (Ph-^{1}DHP). In contrast, with the 4-(3-nitrophenyl) derivative no fluorescence was observed at room temperature, a result attributed to intramolecular electron transfer (ET) between the two moieties present to give the zwitterion 3-NO_2Ph$^{\bullet -}$-DHP$^{\bullet +}$. In a glassy matrix at 77 K, a phosphorescence attributable to a localized triplet (3-NO_2-Ph-^{3}DHP) was observed, despite the fact that ISC from ^{1}DHP to ^{3}DHP was negligible (indeed no phosphorescence was observed from 4-unsubstituted DHP). It was suggested that this resulted from intramolecular ET to 3-NO_2Ph$^{\bullet -}$-DHP$^{\bullet +}$ followed by back electron transfer to the DHP localized triplet, favored by the fact that in matrix the zwitterion was higher in energy than in solution, due to the missing stabilization by solvation.

This simple dyad seemed worth further examination in view of the many variations that could be introduced by taking advantage of the Hantzsch synthesis.

CHART 1



Results

In the present work, the luminescence of a series of DHP derivatives bearing an aryl group in 4 (**1**−**3**) was examined. The aryl group introduced was chosen in such a way that the singlet excited state (^{1}Ar) was in any case higher than ^{1}DHP, while the triplet (^{3}Ar) could be either higher or lower than ^{3}DHP; furthermore, structures where photoinduced electron transfer between the two moieties was predicted (by the Weller equation) to be either endo- or exoergonic were included (see below). The compounds studied are shown in Chart 1 and included phenyl, naphthyl, and phenanthryl derivatives with various electron-withdrawing substituents. Some of these compounds had been previously reported and some were purposely synthesized; in every case, the samples were prepared via the Hantzsch synthesis as detailed in the Experimental Section.

In the series of phenyl derivatives **1** various substituents were introduced in position 3 in order to modulate the electron-accepting properties. Presumably the same results would be obtained with the same substituents in position 4 and, in order to have an indication of this point, a 4-substituted derivative, compound **1e**, was also examined. For the sake of comparison, the 4-methyl-1,4-dihydropyridine **4**, lacking the aryl substituent, was examined under the same conditions. In every case, the absorption spectrum was

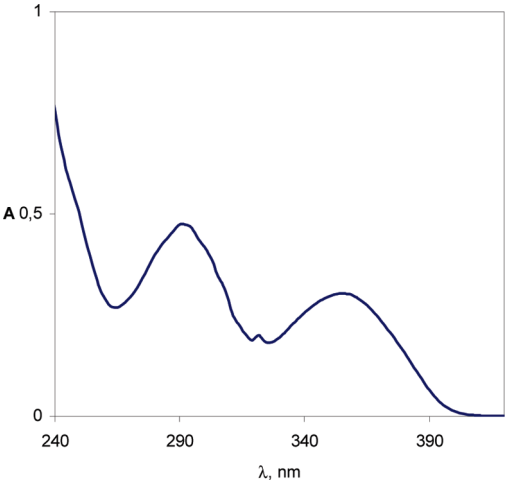


FIGURE 1. Absorption spectrum of dihydropyridine **2a** in acetonitrile (2×10^{-4} M, optical path 1 cm).

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TABLE 1. Prompt Emission for 4-Substituted 1,4-Dihydropyridines 1−4

		MeCN, 293 K		glycerin,[a] 293 K		EPA,[b] 77 K	
compd	4-substituent	λ_{em}	Φ_f	λ_{em}	Φ_f	λ_{em}	Φ_f
4	Me	414, 436	0.006	445	0.27		0.8
1a	Ph	414, 436	0.005	442	0.33	410, 435	0.8
1b	Ph-3-CHO					410, 436	0.22
1c	Ph-3-COPh	416, 434	0.003	442	0.07	410, 435	0.24
1d	Ph-3-NO_2	very weak					
1e	Ph-4-NO_2	very weak					
1f	Ph-3-CH=$CHCO_2Me$	413, 436	0.004			410, 435	0.18
2a	1-Np	416, 436	0.008	442	0.34		0.35
2b	1-Np-4-CN	473	0.043	448	0.03	433, 452	0.22
3	9-Phen	418, 438	0.003			407, 429	0.8

[a]Containing 5% methanol. [b]Diethyl ether−pentane−ethyl alcohol 5−5−2.

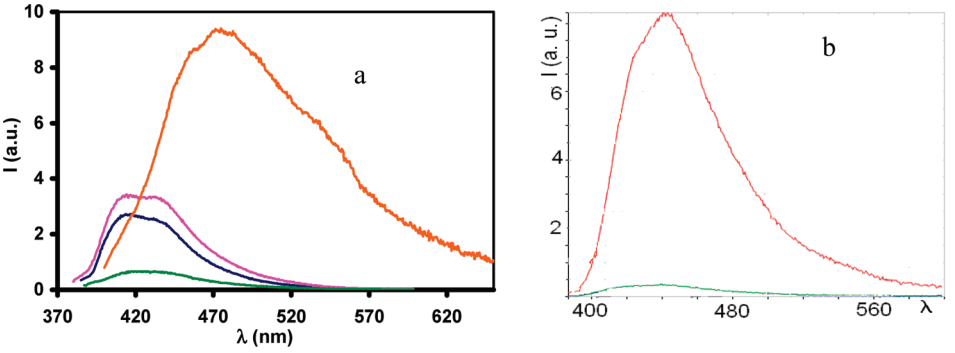

FIGURE 2. Fluorescence spectra of (a) dihydropyridines **1a** (blue), **1c** (green), **2b** (red), and **4** (magenta) in acetonitrile at 20 °C and (b) dihydropyridine **2a** 1×10^{-4} M in ethanol (green) and in glycerine (red) at 20 °C, λ_{exc} 295 nm.

identical with the sum of the spectra of suitable models with a single chromophore, e.g., the spectrum of the naphthyl derivative **2a** (see Figure 1) was undistinguishable from the point-to-point addition of those of compound **4** and 1-methylnaphthalene. This had been previously observed[8] for the case of a pair of phenyl-DHP and is general for the present compounds. Thus, it can be concluded that there is no mutual interaction between the two chromophores in the ground state. As a consequence of the choice of the aryl substituents (high-lying ^{1}Ar state), with all of the compounds it was possible to distinguish at the red end of the spectrum a region where the DHP chromophore was exclusively excited (around 360 nm for **2a** in Figure 1). On the other hand, DHP has a minimum around 290 nm ($\varepsilon_{290} < 0.1\varepsilon_{360}$) where most of the Ar chromophores considered absorb intensively (see Figure 1). This makes it possible to guarantee excitation of the last moiety.

A few 4-phenyl-1,4-dihydropyridines, including **1a**, had been previously examined and found to be weakly fluorescent in solution,[3,9] with emission maxima at ca. 415 and 435 nm and emission quantum yield ≪0.01. Excitation of the present 4-aryl derivatives at 360 nm, where only the DHP chromophore absorbs, gave a similar result, with an even lower Φ_F (see Table 1) and a short lifetime, $\tau_F \ll 1$ ns. With the nitrophenyl derivatives **1d**,**e** the emission was all but undetectable.

Irradiation at 290−300 nm or at 260 nm, where with all of these compounds, except **1a**, the aryl chromophores

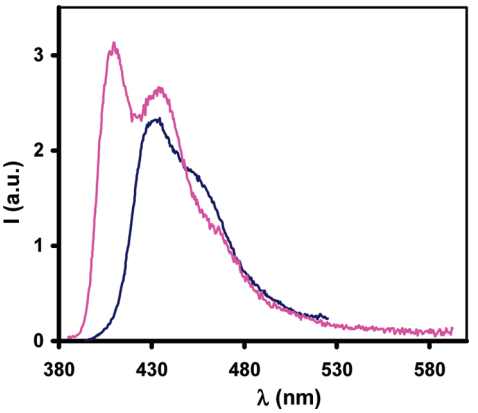

FIGURE 3. Fluorescence spectra of dihydropyridines **2b** (blue) and **3** (magenta) in ether−pentane−alcohol at 77 K, λ_{exc} 300 nm.

contributed ≫50% to the absorption (e.g., benzoylphenyl, naphthyl, phenanthryl), led to no different emission. The only exception among the cases considered was that of the (4-cyanonaphthyl) derivative **2b**, where a more intense emission, with a profile different from that of both DHP and 1-cyanonaphthalene, was observed (see Figure 2a). This had a longer lifetime, τ_F 1.3 ns.

The effect of the solvent was investigated. Apparently, polarity or proticity had no major effect, with essentially the same emission in cyclohexane, ethyl acetate, and ethanol. However, viscous solvents changed the result and with some of these compounds the fluorescence largely increased in glycerin. In this solvent the emission was somewhat

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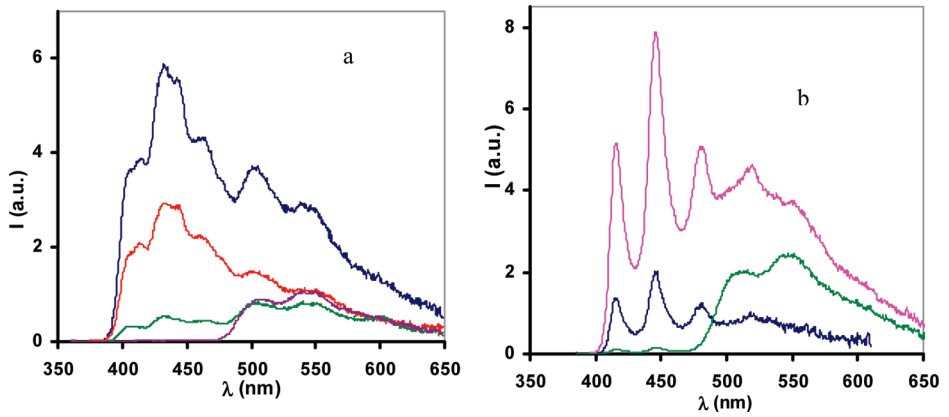


FIGURE 4. Phosphorescence spectra of dihydropyridines (a) **1b** by irradiation at 266 (red), 300 (blue), 320 (green), and 360 nm (violet) and (b) **1c** by irradiation at 266 (magenta), 300 (blue), and 360 nm (green) in ether−pentane−alcohol at 77 K.

red-shifted, more intensive (by a factor > 30) (see Figure 2b), and longer lived, e.g., τ_F increased from ≪1 to 1.8 ns in the case of **2a**. The intensity increment was less marked for the benzoylphenyl derivative **1c** and did not take place with the nitro compounds, where fluorescence remained almost undetectable. As for the cyanonaphthyl derivative **2b**, its peculiar emission was not strengthened in glycerin.

The luminescence in a glassy matrix, ether−pentane−alcohol glass at 77 K, was then examined. As for the prompt emission, this was more clearly vibrationalized under these conditions, but had essentially the same shape as the blue fluorescence in solution at 20 °C. What was different was the intensity. This was much higher and indeed approached a unitary quantum yield for some compounds, such as **1a** and **3**, while with others, in particular the nitrophenyl derivatives, it remained quite low. The spectra reported in Figure 3 result from irradiation at 360 nm, but again irradiation at 300 nm produced no new emission. The cyanonaphthyl derivative **2b** exhibited an emission of its own, at shorter wavelength than at room temperature, and likewise independent of λ_{exc}.

The phosphorescence was likewise examined under the same conditions and was rather varied among the compounds examined. The phenyl derivative **1a** exhibited only a weak phosphorescence, practically the same as the methyl derivative **4**. When an aldehyde or ketone chromophore was present in the acceptor moiety, as in **1b**,**c**, the result depended on the irradiation wavelength. At shorter λ_{exc}, where most of the light was absorbed by the aromatic carbonyl, the typical vibrationalized emission of the benzaldehyde or benzophenone chromophore was the main component. The decay of such emission was similar to that measured with the corresponding carbonyl under the same conditions. On the contrary, irradiation at a longer wavelength, where the DHP chromophore was mainly or exclusively excited, generated a different, and somewhat longer lived, emission at ca. 510, 540 nm (Figure 4a,b).

As for the nitrophenyl derivatives **1d**,**e**, both of them exhibited a marked phosphorescence that was similar in shape to that obtained with **1b**,**c** by 360 nm irradiation (see Figure 5), but in this case was observed also by short wavelength irradiation. With **1d**,**e** the yellow phosphorescence could be visually appreciated, since, different from the other compounds, it was not mixed with the blue fluorescence.

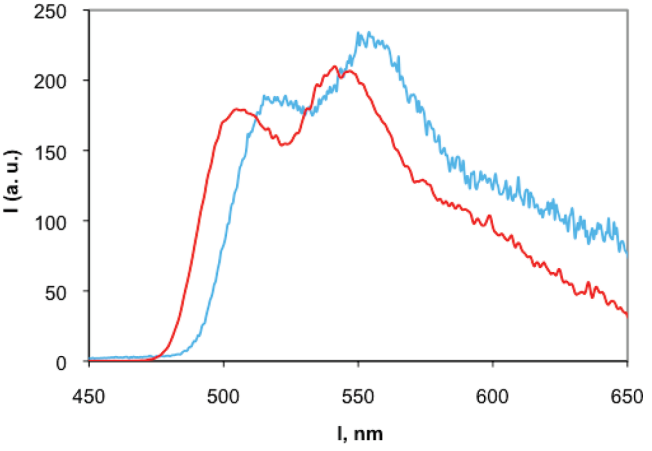


FIGURE 5. Phosphorescence spectra of nitrophenyldihydropyridine **1d** (red) and **1e** (blue) in ether−pentane−alcohol at 77 K, λ_{exc} 300 nm.

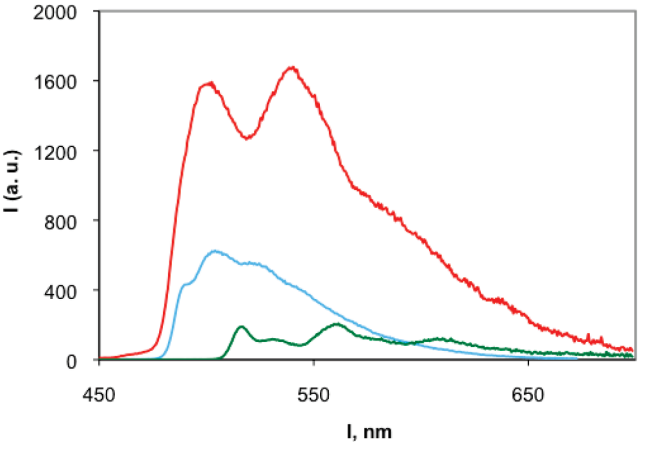


FIGURE 6. Phosphorescence spectra of dihydropyridines **2a** (blue), **2b** (green), and **3** (red) in ether−pentane−alcohol at 77 K, λ_{exc} 300 nm.

The ethoxycarbonylvinylphenyl DHP **1f**, on the other hand, exhibited no phosphorescence at all.

A long-lived yellow emission with maxima around 500 and 540 nm, similar to that of **1b**−**e**, was exhibited also by the

TABLE 2. Delayed Emission for 4-Substituted 1,4-Dihydropyridines 1−3 in Ether−Pentane−Alcohol at 77 K[a]

compd	4-substituent	λ_{em}[b]	E_T,[c] kcal/mol
1b	Ph-3-CHO	508, 544[d] 412, 432,462[e]	59.7
1c	Ph-3-COPh	514, 547[d] 428, 446, 481, 521[e]	59.6
1d	Ph-3-NO_2	513, 547	
1e	Ph-4-NO_2	520, 555	
1f	Ph-3-CH=$CHCO_2$Me	none	
2a	1-Np	490, 504, 521	59.7
2b	1-Np-4-CN	516, 562, 611	56.6
3	9-Phen	502, 540	60.2

[a]In diethyl ether−pentane−ethyl alcohol 5−5−2. [b]When not otherwise stated, independent of λ_{exc}. [c]The energy of triplet ^{3}ArH is taken as an indication of that of the localized DHP-^{3}Ar triplet. [d]By irradiation at 360 nm. [e]By irradiation at 300 nm.

phenanthryl derivative (**3**, see Figure 6; Table 2). With the naphthyl derivative the emission was again similar, but weaker and somewhat blue-shifted (see Figure 6). In contrast, with the cyanonaphthyl substituted derivative **2b** a different greenisch phosphorescence with a marked vibrational strucutre was recorded. This was identical with that obtained from an authentic sample of 1-cyanonaphthalene. With all of these compounds, the observed emission did not depend on the excitation wavelength.

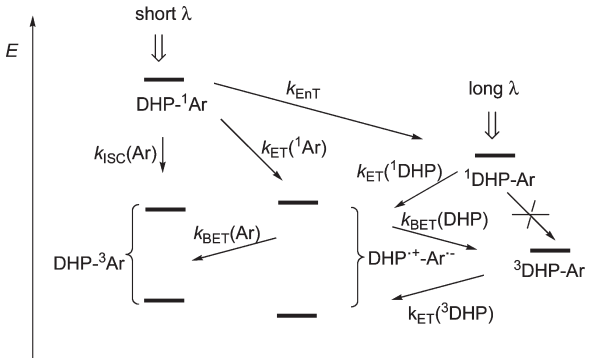
Some ancillary experiments were carried out. In particular, it was tested whether the DHP and aryl moieties interacted also intermolecularly, when the chromophores were in separated molecules. Thus, it was observed that the fluorescence of dihydropyridine **4** was minimally quenched by arenes, such as naphthalene or phenanthrene. A significant quenching was observed with 1-cyanonaphthalene and nitrobenzene (K_{SV} = 3 and 32 M^{-1} respectively in ethanol at 20 °C). A preliminary test on the photochemical reactivity of these compounds was carried out and it was found that none of them was highly reactive ($\Phi_r < 0.01$), except for **1f**, which appeared to undergo geometric isomerization.

Discussion

In the dyads we considered, an aromatic moiety is present and separated from the DHP chromophore by a sp^3 carbon (DHP-Ar). In these compounds, donor and acceptor moieties are ca. 6 Å apart and are held in a roughly perpendicular position by the bulk of the two ester groups.[3,7] There is no significant interaction between the two moieties in the ground state, and the absorption of each compound corresponds to the sum of those of the two separated chromophores. However, the data above show a quite varied panorama in the luminescence of such aryldihydropyridines, revealing that electronic excitation may lead to a different end result.

Considering first the DHP moiety, it is known that the intense absorption by this chromophore at ca. 350 nm ($\log \varepsilon \approx 4$) corresponds to an allowed transition with internal charge transfer character, with calculated $f = 0.1$.[8] The corresponding "natural" fluorescence lifetime is around 10 ns. However, as indicated above, the lifetime measured in solution is well below 1 ns. This is due to internal conversion promoted by rapid conformational equilibrium of the nonrigid dihydropyridine skeleton. A clear support for this rationalization comes from the increase of both intensity and lifetime in going to a viscous solvent as glycerin or to a glassy state at 77 K. The two situations are not equivalent, as is apparent when comparing the spectra. As an example compound **1a** (and similarly **4**) exhibits a broadband beginning at 395 nm and with a maximum around 442 nm in glycerin, somewhat red-shifted with respect to nonviscous liquids. In EPA glass at 77 K the spectrum is vibrationalized (λ_{max} = 410, 435 nm) but not red-shifted with respect to a fluid solution at room temperature. These results suggest that, besides the freezing of conformational equilibria due to the high viscosity, there is also a specific stabilization in glycerin, not in EPA glass. The large increase of fluorescence is not accompanied by a significant phosphorescence in viscous or glassy media with the above derivatives, in accord with the notion that ISC within the DHP moiety (^{1}DHP-Ar to ^{3}DHP-Ar) has no role.

SCHEME 2. Photoinduced Electron and Energy Transfer in DHP-Ar Dyads[a]



[a]The range of variation of the aryl localized triplets (DHP-^{3}Ar) and radical ion pairs (DHP$^{\bullet+}$-Ar$^{\bullet-}$) is indicated.

As for the aryl moiety, this was chosen in such a way that in every case the singlet lies higher in energy than ^{1}DHP, thus long-wavelength irradiation gave ^{1}DHP-Ar. With all of the derivatives tested, except **1a**, irradiation at ca. 300 nm, where the absorptivity of DHP is low ($\varepsilon < 10^2$), makes possible the selective, or at least predominant, excitation of the Ar chromophore. Thus, it is also possible to have DHP-^{1}Ar as the initial state. However, no fluorescence from such chromophores is observed, neither in fluid solution nor in a rigid matrix. This can be due either to an intrachromophore or to an interchromophore process. In the first case the localized singlet is rapidly depopulated, typically because of a fast ISC from ^{1}Ar to ^{3}Ar, as one would expect with the aromatic carbonyls **1b**,**c**. As for the latter one, an expected process is efficient singlet−singlet energy transfer (k_{EnT}, see Scheme 2) leading to the locally excited ^{1}DHP-Ar state (the lowest lying singlet). This does not lead to increased fluorescence, because, as mentioned above, dihydropyridines emit poorly in fluid solution. However, one can judge whether ^{1}DHP-Ar is formed from the emission in viscous or frozen media, as is apparent in the strong blue fluorescence observed with hydrocarbon-substituted dyads **1a**, **2a**, and **3**.

Alternatively, electron transfer (k_{ET}, Scheme 2) between the two moieties may have a role. For several of the aromatic systems considered electron transfer (ET) from ^{1}DHP to the aromatics (eq 1) to form solvent separated radical ion pairs is largely exoergonic in the monochromophoric

TABLE 3. Calculated Free Energy Change for Electron Transfer Processes and Energy of the Solvent Separated Radical Ion Pair (SSRIP)[a]

			ΔG_{ET}			
compd	4-substituent	E_T(Ar)	^{1}DHP → Ar	^{3}DHP → Ar	^{3}Ar → DHP	SSRIP, kcal/mol
1b	Ph-3-CHO	71.7	−11.6	1.2	−10.3	61.3
1c	Ph-3-COPh	68.1	−12.7	0	−8.3	60.2
1d/**1e**	Ph-3(4)-NO_2	∼62	−26.1	−13.3	15.9	46.8
1f	Ph-3-CH=$CHCO_2$Me	54.8	−10.4	2.4	7.8	62.5
2a	1-Np	61.4	3.8	16.7	15.5	76.8
2b	1-Np-4-CN	58.0	−11.7	1.2	3.4	61.3
3	9-Phen	61.6	0.2	13	11.6	73.1

[a]The required data were taken from the literature. E_T(Ar) (in kcal/mol): Ar = 3-MePhCHO, 71.7;[10a] 3-MePhCOPh, 68.1;[10a] 3-MePhNO_2, 62.8;[10b] PhCH=$CHCO_2$Me, 54.8;[10c] 1-MeNp, 61.4;[10d] Np-1-CN, 58.0;[10d] Phen, 61.6;[10e] DHP, 60.2.[3] E_{red}(Ar) (V vs. SCE): Ar = 3-MePhCHO, −1.88;[10f] 3-MePhCOPh, −1.83;[10g] PhNO_2, −1.17;[10h] PhCH=$CHCO_2$Me, −1.93;[10i] 1-MeNp, −2.55; [10j] Np-4-CN, −1.88;[10d] Phen, −2.39.[10k] E_{ox}(DHP), see refs 3 and 10l.

analogues ArH (see Table 3)

$$^1\text{DHPH} + \text{ArH} \rightarrow \text{DHPH}^{\bullet+} + \text{ArH}^{\bullet-} \quad (1)$$

Due to the short lifetime of the dihydropyridines singlet, intermolecular ET occurs only at high concentrations of the quencher, as shown by the low or moderate Stern−Volmer constants. When the two moieties are held closely as in the present dyads, however, intramolecular electron transfer is facile and a tethered radical ion pair is formed (RIP, k_{ET}, see eq 2)

$$^1\text{DHP-Ar} \rightarrow \text{DHP}^{\bullet+}\text{-Ar}^{\bullet-} \quad (2)$$

Thus, it is expected that ET has a large role when the aryl group is easily reduced, that is when it bears a carbonyl, nitro, cyano, or acrylate substituent. A particular case is that of the cyanonaphthyl derivative **2b**, with which a new emission is observed rather than more quenching. Apparently, an exciplex is formed. Both the emission intensity and the lifetime are larger than those of localized excited states that are formed in other dyads.

$$^1\text{DHP-Ar} \rightarrow (\text{DHP}^{\delta+}\text{-Ar}^{\delta-}) \quad (3)$$

The formation of such an exciplex must have geometric requirements, as indicated by the blue-shifted emission in glycerin and in EPA glass with respect to the fluid solution, suggesting that the electronic structure is less perturbed with respect to localized ^{1}DHP-Ar. Emitting exciplexes between 1-cyanonapthalene and aromatics are not known; however, when the two moieties are tethered emission is favored, as already demonstrated for 1-cyanonaphthalene−alkenes exciplexes.[11]

The processes considered up to now (see Scheme 2) lead to either ^{1}DHP-Ar, the RIP (nonemitting except for the case of **2b**), or DHP-^{3}Ar. Subsequent processes can be envisaged. For example, ET from ^{3}Ar to DHP is possible for the carbonyl derivatives (see Table 3) and gives again the RIP (analogously to eq 3). The RIP formed from any of the above paths may undergo ISC to give, provided that this is thermodynamically allowed, the lowest localized triplet (eq 4).

$$(\text{DHP}^{\delta+}\text{-Ar}^{\delta-})/\text{DHP}^{\bullet+}\text{-Ar}^{\bullet-} \rightarrow {}^3\text{DHP-Ar or DHP-}{}^3\text{Ar} \quad (4)$$

Taking into account that the energy of the localized dihydropyridine triplet ^{3}DHP-Ar is ca. 60 kcal/mol (see Table 2) and the variable energy of ^{3}Ar and the RIP according to the nature of Ar, different situations can be recognized, as illustrated below (see Scheme 2 and Table 3; notice, however, that the SSRIP energy values reported in the table refer to fluid solution and are not exactly representative of the situation in the glass).

With the naphthyl (**2a**) and phenanthryl (**3**) derivatives both ^{1}DHP fluorescence and ^{3}DHP phosphorescence are observed and are independent of the excitation wavelength. The singlet excited states of aromatic hydrocarbons have a lifetime on the order of tens of nanoseconds essentially determined by ISC [k_{ISC}(Ar)]. This long lifetime makes quenching of ^{1}Ar within the dyad complete. This involves in part energy transfer (EnT), as evidenced by the ^{1}DHP-Ar fluorescence, in part ET, barely possible and thus inefficient with the naphthyl derivative, while k_{ISC}(Ar) has no role [k_{ISC}(Ar) < k_{EnT}(Ar), k_{ET}(Ar)]. Of the two localized triplets, ^{3}DHP-Ar is formed through back electron transfer from the RIP [k_{BET}(DHP)] as revealed by the phosphorescence. It is possible that the about isoenergetic DHP-^{3}Ar is likewise formed from the RIP and is in equilibrium, but due to the small emission rate constant typical of hydrocarbon triplets gives rise to no detectable emission (see Table 4).

With aromatic aldehydes and ketones the k_{ISC}(Ar) is larger. Thus, when **1b**,**c** are irradiated in the aryl chromophore, the short lifetime of ^{1}Ar allows only for partial energy transfer in the singlet and the main process in the dyad remains intersystem crossing as in the isolated ArH molecule. Thus, DHP-^{3}Ar is formed [k_{ISC}(Ar) > k_{EnT}(Ar), k_{ET}(Ar)] and revealed by the phosphorescence (see experiments by short wavelength irradiation). As shown in Table 3, the Ar localized triplet could not be formed from other paths. On the other hand, selective excitation in the DHP region is followed by the greatly favored ET to the RIP [k_{ET}(^{1}DHP)] and back ET to give the localized ^{3}DHP-Ar, the most stable triplet.

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TABLE 4. Paths Followed upon Photoexcitation of Dyads 1−3[a,b]

compd	4-substituent	processes occurring
1b,**c**	Ph-COR	(a) DHP-^{1}Ar → DHP-^{3}Ar (**P**) (b) DHP-^{1}Ar → DHP$^{\bullet+}$-Ar$^{\bullet-}$ → ^{3}DHP-Ar (**P**) (c) ^{1}DHP-Ar → DHP$^{\bullet+}$-Ar$^{\bullet-}$ → ^{3}DHP-Ar (**P**)
1d	Ph-3-NO_2	DHP-^{1}Ar → DHP$^{\bullet+}$-Ar$^{\bullet-}$ → ^{3}DHP-Ar (**P**)[c,d]
1f	Ph-3-CH=CHCO_2Me	DHP-^{1}Ar → DHP$^{\bullet+}$-Ar$^{\bullet-}$ → DHP-^{3}Ar[c]
2a, **3**	1-Np, 9-Phen	DHP-^{1}Ar → DHP$^{\bullet+}$-Ar$^{\bullet-}$ → ^{3}DHP-Ar (**P**)[c]
2b	1-Np-4-CN	DHP-^{1}Ar → DHP$^{\bullet+}$-Ar$^{\bullet-}$ (**F**) → DHP-^{3}Ar (**P**)[c]

[a]**F**, **P**: fluorescence or respectively phosphorescence detected from the species indicated. [b]Besides emission from directly excited ^{1}DHP (**F**) and the process DHP-^{1}Ar → ^{1}DHP-Ar (**F**), observed with all of these compounds, except where noted. [c]Same process occurring also starting from ^{1}DHP-Ar. [d]No ^{1}DHP fluorescence observed.

With the nitrophenyl derivatives **1d**,**e** ET from ^{1,3}DHP to Ar is markedly exoergonic, although in matrix not as much as in solution, and the ^{1,3}Ar localized states are nonemitting. Thus, emssion is due only to DHP localized states. Fluorescence is detected neither in fluid solution nor in glass, but in the latter case phosphorescence is apparent. Thus, ET is the main process, both when the nitrobenzene chromophore is irradiated [k_{ISC}(Ar) < k_{ET}(^{1}Ar)] and when DHP is irradiated [k_{IC}(DHP) < k_{ET}(^{1}DHP)]. In the glassy solution where phosphorescence is measured the RIPs in the dyad are not as stabilized as the free molecules in solution, and BET gives ^{3}DHP-Ar [k_{BET}(DHP)], apparently the most stable triplet (although formation of some DHP-^{3}Ar cannot be discounted, since this would not emit and thus would escape detection). Notice that the phosphorescence spectra detected with several of the above dyads and attributed to ^{3}DHP are similar, but not identical. Thus, the final state may be either "pure" ^{3}DHP-Ar or an exciplex with the excitation mainly on the DHP moiety.

As for cynnamate **1f**, this has a low-lying, nonemissive triplet (because of the competition with fast geometrical isomerization). As a result, a little DHP fluorescence is observed, but exoergonic ET is the main process from the singlet [k_{ISC}(Ar), k_{EnT}(^{1}Ar) < k_{ET}(^{1}Ar) and analogously for ^{1}DHP]. As for the triplet multiplicity, the system inevitably evolves to DHP-^{3}Ar (k_{BET}(Ar) predominating) and thus no long-lived emission occurs. The situation of compound **2b** bearing a cyanonaphthalene substituent is in part similar, again with ET predominating from both ^{1}Ar and ^{1}DHP and BET leading to DHP-^{3}Ar, with the important difference that both the RIP (in fluid solution) and DHP-^{3}Ar (in glass) emit and are in fact directly detected.

The general features of the light-induced processes of the DHP-Ar dyads are summarized in Table 4, where the processes occurring on irradiating either of the two chromophores are indicated, along with the luminescence detected (fluorescence from ^{1}DHP, observed in most cases, is not indicated for the sake of simplicity).

Conclusion

The above data evidence the versatility of the DHP-based dyads, in the sense that energy and electron transfer are directed by the structure. Thus, one can engineer these systems in such a way that upon excitation of either component, the energy can be finally deposited on either component, DHP or Ar, by the rational planning of the intradyad steps, or at least this is possible for the triplet states. Key parameters are triplet energy and reduction potential of the chosen Ar group that must be compared with the fixed triplet energy and oxidation potential of DHP. Scheme 2 illustrates how the position of ^{3}Ar and of the RIP (DHP$^{\bullet+}$-Ar$^{\bullet-}$) vary within the brackets indicated and correspondingly how vary their position relative to ^{3}DHP, governing the evolution of the system. Splitting is possible, as illustrated by the case of the fast ISC in carbonyl derivatives **1b**,**c** that diminishes, but does not completely hinder, ET from DHP.

Considered along with the easy and versatile synthesis of dihydropyridines, these results suggest that such systems can be considered among the most useful for the elaboration of fully organic dyads for the vectorial transport of energy or charge tranfer. In the present study, emission is used as a diagnostic tool of the processes occurring. However, if the limitation of the poor emission in fluid solution is overcome, DHP-based dyads may be developed as versatile sensors too.

Experimental Section

Compound **4** was of commercial origin. Compounds **1a**,**d**,**e** were prepared and purified as previously reported.[7] The other 1,4-dihydropyridines were prepared through the Hatzsch synthesis as detailed below. Chromatographic separations were carried out on silica gel eluting with cyclohexane−ethyl acetate mixtures. Samples for spectroscopic examination were repeatedly crystallized until a constant mp was reached.

Dimethyl 1,4-Dihydro-2,6-dimethyl-4-(3-formylphenyl)-3,5-dicarboxylate (1b). Isophthaladehyde (1.99 g, 14.1 mmol) and methyl acetacetate (3.36 mL, 3.11 mmol) were dissolved in 10 mL of methanol, 1.1 mL of 30% aqueous ammonia was added, and the mixture was refluxed for 4 h, when TLC showed that the starting material has been consumed. Separation by chromatography and repeated crystallization gave the title compound as a slightly yellow solid (0.075 g, 5% yield, mp 260 °C). ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 6H), 3.66 (s, 6H), 5.10 (s, 1H), 5.71 (s, 1H, exch), 7.42 (t, 1H, J = 7 Hz), 7.60 (d, 1H, J = 7 Hz), 7.67 (d, 1H, J = 7 Hz), 7.77 (br s, 1H), 9.98 (s, 1H); ^{13}C ($CDCl_3$) δ 19.6 (CH_3), 39.4 (CH), 51.0 (CH_3), 103.5, 128.0 (CH), 128.5 (CH), 128.7 (CH), 134.1 (CH), 136.4, 144.4, 148.6, 167.6, 192.6 (CH). IR (KBr) 3220, 1700 cm^{-1}. Anal. Calcd for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.81; N, 4.25. Found C, 65.4; H, 6.0; N, 4.1.

Dimethyl 1,4-Dihydro-2,6-dimethyl-4-(3-benzoylphenyl)-3,5-dicarboxylate (1c).[12] 3-Benzoylbenzaldehyde (0.50 g, 2.35 mmol) and methyl acetacetate (0.55 mL, 5.2 mmol) were disssolved in methanol (1.4 mL), 30% aqueous ammonia was added (0.2 mL), and the solution was refluxed for 4 h, when TLC showed that the starting material had been consumed. Separation by column chromatography and crystallization gave the title compound as a colorless solid (0.41 g, 44% yield, mp 150−151 °C). ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 6H), 3.68 (s, 6H), 5.08 (s, 1H), 5.89 (s, 1H, exch), 7.35 (t, 2H, J = 7 Hz), 7.43−7.55 (m, 2H), 7.55−7.65 (m, 2H), 7.72 (br s, 1H), 7.8 (d, 2H, J = 7 Hz); ^{13}C ($CDCl_3$) δ 19.4 (CH_3), 39.3 (CH), 51.0 (CH_3), 103.4, 127.9 (CH), 128.0 (2 CH),

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129.1 (CH), 129.5 (CH), 130.0 (2 CH), 132.0 (CH), 132.2 (CH), 137.1, 137.7, 144.5, 147.7, 167.7, 196.9. IR (KBr) 3240, 1690, 1665 cm^{-1}. Anal. Calcd for $C_{24}H_{23}NO_5$: C, 71.10; H, 5.72; N, 3.45. Found: C, 70.9; H, 5.7; N, 3.3.

(*Z*)-Methyl 3-{3-[4-(1,4-Dihydro-2,6-dimethyl-3,5-dimethoxycarboxyl)]}propenoate (1f). Methyl 3-(3-formylphenyl)acrylate (0.35 g, 2.0 mmol)[13] and methyl acetacetate (0.45 mL, 4.2 mmol) were dissolved in methanol (1.1 mL), 30% aqueous ammonia was added (0.2 mL), and the solution was refluxed for 3 h, when TLC showed that the starting material had been consumed. Separation by column chromatography and crystallization gave the title compound as a colorless solid (0.40 g, 82% yield, mp 155 °C). ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 6H), 3.66 (s, 6H), 3.82 (s, 3H), 5.03 (s, 1H), 6.12 (s, 1H, exch), 6.39 (d, 1H, J = 16 Hz), 7.20−7.35 (m, 3H), 7.44 (br s, 1H), 7.68 (d, 1H, J = 16 Hz); ^{13}C NMR ($CDCl_3$) δ 29.6 (CH_3), 39.3 (CH), 50.5 (CH_3), 55.6 (CH_3), 103.4, 116.0 (CH), 125.6 (CH), 127.8 (CH), 128.4 (CH), 129.9 (CH), 134.0, 144.6, 145.5 (CH), 148.2, 162.6, 162.8. IR (KBr) 3240, 1690, 1665 cm^{-1}. Anal. Calcd for $C_{21}H_{23}NO_6$: C, 65.44; H, 6.02; N, 3.63. Found: C, 65.7; H, 6.0; N, 3.4.

Dimethyl 1,4-Dihydro-2,6-dimethyl-4-(1-naphthyl)-3,5-dicarboxylate (2a).[14] 1-Naphthylaldehyde (2.87 g, 18.4 mmol) and methyl acetacetate (4.4 mL, 40.5 mmol) were dissolved in methanol (11 mL), 30% aqueous ammonia was added (1.5 mL), and the solution was refluxed for 5 h, when TLC showed that the starting material had been consumed. Separation by column chromatography and crystallization gave the title compound as a colorless solid (0.80 g, 13% yield, mp 248−249 °C). ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 6H), 3.43 (s, 6H), 5.73 (s, 1H), 5.84 (s, 1H, exch), 7.35 (t, 2H), 7.45 (m, 3H), 7.55 (m 2H), 7.63 (d, 1H, J = 8 Hz), 7.78 (d, 1H, J = 8 Hz), 8.58 (d, 1H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 19.4 (CH_3), 39.3 (CH), 50.6 (CH_3), 105.4, 124.9 (CH), 125.0 (CH), 125.05 (CH), 125.6 (CH), 126.8 (CH), 127.0 (CH), 127.9 (CH), 130.7, 133.1, 143.3, 146.5, 168.7. IR (KBr) 3240, 1670 cm^{-1}. Anal. Calcd for $C_{21}H_{21}NO_4$; C 71.78; H, 6.02; N, 3.99. Found: C, 72.0; H, 6.1; N, 3.8.

Dimethyl 1,4-Dihydro-2,6-dimethyl-4-[1-(4-cyanonaphthyl)]-3,5-dicarboxylate (2b). 4-Cyanonaphthalene-1-carboxyaldehyde (0.46 g, 2.5 mmol) and methyl acetacetate (0.65 mL, 5.6 mmol) were disssolved in methanol (1.5 mL), 30% aqueous ammonia was added (0.2 mL), and the solution was refluxed for 5 h, when TLC showed that the starting material had been consumed. Separation by column chromatography and crystallization gave the title compound as a yellow solid (0.18 g, 20% yield, mp 218−220 °C). ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 6H), 3.38 (s, 6H), 5.81 (s, 1H, exch), 5.89 (s, 1H), 7.65 (d, 1H, J = 8 Hz), 7.7 (m, 2H), 7.8 (d, 1H, J = 8 Hz), 8.1 (m, 1H), 8.75 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 19.5 (2 CH_3), 35.2 (CH), 50.7 (2 CH_3), 104.7, 108.3, 118.3, 125.9 (CH), 126.2 (CH), 126.5 (CH), 127.7 (CH), 130.4, 132.2, 132.6 (CH), 144.0, 152.8, 167.5. IR (KBr) 3240, 2210, 1690 cm^{-1}. Anal. Calcd for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.57; N, 7.44. Found: C, 70.4; H, 5.7; N, 7.2.

Dimethyl 1,4-Dihydro-2,6-dimethyl-4-(9-phenanthryl)-3,5-dicarboxylate (3).[15] 9-Phenanthenecarboxyaldehyde (0.56 g, 2.7 mmol) and methyl acetacetate (0.70 mL, 5.1 mmol) were disssolved in methanol (1.6 mL), 30% aqueous ammonia was added (0.2 mL), and the solution was refluxed for 4 h 30 min, when TLC showed that the starting material had been consumed. Separation by column chromatography and recrystallization from methanol gave the title compound as a colorless solid (40 mg, 4%, mp 245 °C). ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 6H), 3.40 (s, 6H), 5.65 (s, 1H, exch), 5.82 (s, 1H), 7.5−7.8 (m, 6H), 8.63−8.70 (m, 3H); ^{13}C NMR ($CDCl_3$) δ19.5 (CH_3), 34.4 (CH), 50.5 (CH_3), 105.6, 122.25 (CH), 122.3 (CH), 125.6 (2 CH), 125.9 (CH), 126.0 (CH), 127.9 (CH), 128.0 (CH), 129.6, 129.8, 130.3, 132.0, 143.0, 145.8, 168.0. IR (KBr) 3300, 2210, 1695 cm^{-1}. Anal. Calcd for $C_{25}H_{23}NO_4$: C, 74.79; H, 5.77; N, 3.49. Found: C, 74.7; H, 5.8; N, 3.4.

Measurements: Luminescence. The luminescence was measured by means of a thermostated pulsed fluorimeter either at 20 °C or at 77K by using the liquid nitrogen fitting. Quantum yields of emission were measured taking quinine bisulfate (Φ_f = 0.546 at room temperature) or carbazole (in glass, Φ_p = 0.24)[16] as standards. The fluorescence lifetime was measured through the single photon counting technique.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra of compounds **1b**, **1c**, **1f**, **2a**, **2b**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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