# Trans-A_B-corroles Bearing a Coumarin Moiety - From Synthesis to Photophysics 

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#### Abstract

Four dyads comprised of corrole and coumarin units have been synthesised. Three coumarincarboxaldehydes were synthesized and transformed into the corresponding trans$\mathrm{A}_{2} \mathrm{~B}$-corroles by reaction with 5-(pentafluorophenyl)dipyrromethane. It has been proven that this type of direct condensation can lead to the corresponding corroles in moderate yields. The reaction of hydroxybenzaldehydes with vinylphosphonium salts has been identified as the most general method


for the preparation of formyl-coumarins with various patterns of substituents. The dyad consisting of ketobiscoumarin and corrole was synthesized by Sonogashira coupling. Spectroscopic and photophysical investigations revealed that there is an efficient energy transfer from the coumarin moiety to

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corrole in all four dyads. Energy transfer can be clearly ascribed to a dipoledipole mechanism (Förster) for all dyads that contain luminescent coumarins and to an electron exchange mechanism (Dexter) for the dyad with the non-luminescent one. In the case of the dyad that bears coumarin with a hydroxy group at position 5, an elec-tron-transfer was detected from corrole to coumarin. The latter process is possible because of the suitably low reduction potential of coumarins of this type.

## Introduction

One of the major objectives in the field of artificial photosynthesis is to create synthetic light-harvesting complexes that are able to convert and store light energy. ${ }^{[1]}$ Numerous artificial photonic assemblies based on multiporphyrin architectures have been designed with the goal of achieving efficient energy and charge transfer. ${ }^{[2]}$ Understanding the factors that control the excited-state energy transfer is essential for the rational design of a wide variety of molecular photonic devices.
Corroles, one carbon short analogues of porphyrins, have recently emerged as an independent area of research. ${ }^{[3]}$ Their coordination chemistry, ${ }^{[4]}$ synthesis, ${ }^{[5]}$ chemical transformations, ${ }^{[6]}$ electrochemistry, ${ }^{[7]}$ and other properties ${ }^{[8]}$ have

[^0]been studied in great detail. In contrast to porphyrins, the photophysics of corroles has scarcely been studied and only recently information regarding the basic photophysical properties of corroles became available ${ }^{[9]}$ and stable dyads that comprise of corrole and other units started to be investigated. ${ }^{[10]}$ As a part of a broader program in the chemistry of corrole containing assemblies, we have created covalently linked corrole-coumarin dyads. Coumarins, as counterpart, were chosen because of their excellent and well documented photochemical and photophysical behavior. ${ }^{[11]}$ Owing to their intense fluorescence, coumarin dyes have attracted considerable interest as laser dyes, ${ }^{[12]}$ as emitter layers in OLEDs, ${ }^{[13]}$ and as optical brighteners. ${ }^{[14]}$ The structure-property relationship of coumarin derivatives has recently been studied in detail. ${ }^{[15-17]}$ On the other hand, coumarins were not extensively used in the construction of light-harvesting model systems, ${ }^{[18]}$ and only a few reports have been published about the photophysical properties of coumarin-porphyrin conjugates. ${ }^{[19]}$

Our aim was to investigate the efficiency of energy transfer between the coumarin and corrole units in covalently linked dyads. Herein, we report the results of our synthetic and photophysical studies.

## Results and Discussion

## Design and Synthesis

Trans- $\mathrm{A}_{2} \mathrm{~B}$-corroles that bear a coumarin moiety attached at the meso-10-position of the corrole were chosen for our studies. This convenient architecture allows the benefit of efficient, general synthetic procedures developed in the last 10 years. We focused our investigation mainly on the relatively simple coumarins that bear electron-donating groups and absorb UV-light. We also designed a corrole bearing a biscoumarin unit that is able to absorb green light. The desire to achieve fast and efficient energy transfer led us to prepare mainly dyads that bear a direct link between both the chromophores. Two pentafluorophenyl units were intended to be introduced at positions 5 and 15 because they secure good photostability of the corrole core for photophysical characterization. ${ }^{[12]}$ Our strategy was to synthesize coumarin-derived aldehydes and then transform them into corroles.
The preparation of the first dyad started from the formylation of vanilin (1) using the Duff reaction to give the dialdehyde 4 (Scheme 1). ${ }^{[20]}$ Subsequently, the dialdehyde 2 was transformed into formyl-coumarin $\mathbf{4}$ under classical Knoevenagel conditions. This aldehyde was reacted ${ }^{[21]}$ with dipyrromethane $\mathbf{3}$ to afford the corrole Cum1-C3 in $4 \%$ yield (Scheme 1). An increase in the concentration of TFA ${ }^{[22]}$ resulted in an increase in yield by up to $15 \%$.

It is well known that the spectroscopic properties of coumarins strongly depend on the presence of electron-donating groups at position $7 .{ }^{[11,17]}$ In consequence, coumarin-corroles that bear an OH group at this position were the main part of our effort.

Formylation of various 7-hydroxycoumarins proved inefficient as a way to prepare the desired aldehydes. In such a situation, we focused on the reaction of phenols with vinylphosphonium salts (formed in situ from DMAD and $\mathrm{PPh}_{3}$ ) that give coumarins. ${ }^{[23]}$ We envisioned that the formyl group present in the substrate would not interfere with the reaction course. We studied this hypothesis by performing the reaction of aldehyde 5 with $\mathrm{DMAD} / \mathrm{PPh}_{3}$ under reported

Abstract in Polish: Cztery układy dwuchromoforowe, skła-
dające się z jednostek korolowych i kumarynowych zsyntety-
zowano poprzez kondensację formylokumaryn z 5-(penta-
fluorofenylo)dipirometanem. Udowodniono, że reakcja al-
dehydów hydroksybenzoesowych z solami winylofosfonio-
wymi jest najbardziej ogólną metodą syntezy formylokuma-
ryn. Badania spektroskopowe i fotofizyczne wykazały
istnienie transferu energii od układu kumaryny do pierście-
nia korolu. Transfer ten zachodzi według mechanizmu För-
stera w przypadku gdy kumaryna wykazuje fluorescencję a
według mechanizmu Dextera dla kumaryny niefluoryzującej.
Dla układu dwuchromoforowego zawierającego kumarynę z
grupą hydroksylową w pozycji 5 zachodzi również transfer
elektronu w kierunku od korolu do kumaryny.


1
2



Scheme 1. Synthesis of dyad Cum1-C3.
conditions (Scheme 2). Analysis of the crude reaction mixture showed the formation of multiple products; however simple crystallization from methanol gave one pure compound.


Scheme 2. Synthesis of dyad Cum2-C3.

The spectroscopic data did not correspond to the expected structure, namely, coumarin bearing a hydroxyl group at position 7, but rather to a compound bearing a hydroxyl group at position 5. This pattern of substituents in coumarins is difficult to obtain using other methods. ${ }^{[24]}$

Aldehyde $\mathbf{6}$ was condensed with dipyrromethane $\mathbf{3}$ to give corrole Cum2-C3 in $6 \%$ yield. In view of the above results, in order to realize the synthesis of coumarin building block that possesses an OH group at position 7, the structure of the substrate had to be modified. Namely, aldehyde $\mathbf{8}^{[25]}$ was subjected to a reaction with vinylphosphonium salts (Scheme 3). According to the expectations, aldehyde 9 was


Scheme 3. Synthesis of dyad Cum3-C3.
formed in appreciable yield. Subsequently, it was condensed with dipyrromethane 3 to form the corrole Cum3-C3 in $3 \%$ yield. The relatively low yields of corroles Cum1-C3, Cum2C3, and Cum3-C3 stem from the possible side reactions, especially Michael addition of pyrrole derivatives to the $\alpha, \beta$ unsaturated system of coumarin.
In order to modulate the absorption of the donor energy, we synthesized a ketobiscoumarin building block that bears stronger electron-donating groups. The complex structure of the designed dyad gave negligible chance for its synthesis by direct condensation of dipyrromethanes with formylketobiscoumarin. Sonogashira reaction was identified as the means to form the link between the chromophores. Ethynyl-corrole $\mathbf{1 1}$ was prepared from aldehyde $\mathbf{1 0}^{[26]}$ and dipyrromethane 3 under $\mathrm{H}_{2} \mathrm{O} / \mathrm{MeOH} / \mathrm{HCl}$ conditions ${ }^{[27]}$ (Scheme 4). The second building block was prepared from aldehyde $\mathbf{1 2}^{[28]}$ and $\beta$-ketoester 13. ${ }^{[29]}$ The final copper-free Sonogashira cou-


Scheme 4. Synthesis of corrole 11.
pling was performed under Otsuka conditions ${ }^{[30]}$ and produced the corrole Cum4-C3 in $30 \%$ yield (Scheme 5).

In order to study the energy transfer in the four prepared coumarin-corroles, we needed suitable models. Coumarin


Scheme 5. Synthesis of dyad Cum4-C3.

Cum3 was synthesized using Yavari procedure from 2-methylresorcinol (7) (Scheme 3). All attempts to prepare the coumarin that possesses an OH group at position 5 (model for dyad Cum2-C3) from 4-methylresorcinol using Yavari method, failed. Consequently, the coumarin Cum2 was obtained directly from aldehyde 6 by the protection of the
formyl group as acetal (Scheme 2). Finally, coumarins Cum1 ${ }^{[31]}$ and Cum4 ${ }^{[29]}$ (Scheme 6) were synthesized using known procedures.


Scheme 6. Structures of the compounds.

## Spectroscopy, Photophysics, and Photoinduced Processes

The synthesized coumarin dyads have been studied with pertinent models, and the formulas of the systems studied are displayed in Scheme 6. The absorption spectra of the dyads Cum1-C3, Cum2-C3, Cum3-C3, and Cum4-C3 are reported in Figure 1 together with the spectra of the pertinent component models C3 and Cum1, Cum2, Cum3, Cum4, respectively. Coumarins Cum 2 and Cum3 display a single band in the UV region, at $297 \mathrm{~nm}\left(\varepsilon=10800 \mathrm{~m}^{-1} \mathrm{~cm}^{-1}\right)$ for Cum2 and at $341 \mathrm{~nm}\left(\varepsilon=9700 \mathrm{~m}^{-1} \mathrm{~cm}^{-1}\right)$ for Cum3. Cum1 exhibits a band at $306 \mathrm{~nm}\left(\varepsilon=14200 \mathrm{~m}^{-1} \mathrm{~cm}^{-1}\right)$ and a shoulder at $360 \mathrm{~nm}\left(\varepsilon=1700 \mathrm{~m}^{-1} \mathrm{~cm}^{-1}\right)$. The absorption band of $\mathbf{C u m 4}$ is at lower energies, $\lambda=446 \mathrm{~nm}$, and has a higher oscillator strength, $\varepsilon=96000 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$. C3, formerly characterized, has a strong Soret band at $419 \mathrm{~nm}\left(\varepsilon=120600 \mathrm{~m}^{-1} \mathrm{~cm}^{-1}\right)$ and lower intensity Q bands at $523,562,617$ and 640 nm ( $10000 \mathrm{~m}^{-1} \mathrm{~cm}^{-1}<\varepsilon<20000 \mathrm{~m}^{-1} \mathrm{~cm}^{-1}$ ). The absorption spectra of the dyads are in good agreement with the superposition of the individual components.

In the UV region, Cum1-C3 displays a band with maximum at 303 nm ascribable to Cum1 absorption. Cum2-C3 has a maximum at 302 nm , which is in good agreement with the band maxima of Cum2, and Cum3-C3 has a broad band at 340 nm , coincident with the Cum3 band. A good additive spectrum can also be detected for Cum4-C3, where connection of the units through a phenylethynyl bridge might have
favoured electronic interactions. On the contrary, Cum4-C3 absorption spectrum displays a broad band with a peak at 435 nm and a clear shoulder at 418 nm , which is clearly identifiable as the band of Cum4 and the band of C3, respectively. A minor difference might be noticed only for the oscillator strength of the coumarin transition, which appears slightly intensified in the dyad (Figure 1d).
In the visible region, the bands of all dyads overlap quite well with the Q bands of corrole C3 but it may be noticed that in all the cases there is a slight change in the lowest energy Q bands in the dyads compared to the corrole. The 617 nm band of the corrole is hypsochromically shifted by 510 nm in the dyads and the 640 nm band is less intense. Though sizeable, the perturbation on the spectroscopic properties are however modest and it can be safely assumed that the components in the dyads are electronically decoupled in all cases.
This allows the study of the properties of the dyads with reference to the models and to derive information on the intramolecular processes within the arrays by comparison with the model properties.


Figure 1. Absorption spectra in toluene of: a) Cum1 (---), C3 (.....), Cum1-C3 (-); b) Cum2 (---), C3 (…), Cum2-C3 (-); c) Cum3 (---), C3 (....), Cum3-C3 (-); d) Cum4 (---), C3 (....), Cum4-C3 (一).

The room temperature luminescence properties of the coumarins and corroles are collected in Table 1. The acetal Cum2 was chosen as the model for Cum2-C3 because of the

Table 1. Luminescence properties of models and dyads in toluene at room temperature.

| Compound | $\lambda_{\text {max }}[\mathrm{nm}]^{[\mathrm{a}]}$ | $\Phi_{\mathrm{fl}}{ }^{\text {[b] }}$ | $\Phi_{\mathrm{fl}}{ }^{[\mathrm{c}]}$ | $\Phi_{\mathrm{fl}}{ }^{[d]}$ | $\tau[\mathrm{ns}]^{[\text {e] }}$ | $\tau[\mathrm{ns}]^{[f]}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C3 | 656 | - | 0.14 | 0.14 | - | 3.8 |
| Cum1 | 459 | 0.009 | - | - | 0.38 | - |
| Cum2 | - | <0.0005 | - | - | - | - |
| Cum3 | 441 | 0.011 | - | - | 0.23 | - |
| Cum4 | 472 | 0.016 | - | - | $\begin{aligned} & 0.05(75 \%),{ }^{[g]} .{ }^{[g]} . \\ & 0.25(75 \%)^{[g]} \end{aligned}$ | - |
| Cum1-C3 | 655 | <0.0005 | 0.13 | 0.13 | <0.005 | 3.7 |
| Cum2-C3 | 648 | <0.0005 | 0.012 | 0.012 | - | 0.44 |
| Cum3-C3 | 648 | <0.0005 | 0.14 | 0.14 | <0.005 | 3.9 |
| Cum4-C3 | 658 | <0.0005 | 0.13 | 0.13 | 0.007 | 3.8 |

[a] $\lambda_{\text {max }}$ of emission in toluene, uncorrected spectra. [b] Luminescence quantum yields of coumarins in air equilibrated toluene, excitation on the coumarin band in the UV region. [c] Luminescence quantum yields of corrole, excitation on the coumarin band in the UV region. [d] Luminescence quantum yields of corrole, selective excitation of corrole at 563 nm [e] Fluorescence lifetimes in air equilibrated toluene measured at the coumarin maxima, excitation at 355 nm . [f] Fluorescence lifetimes of corrole in air equilibrated toluene, excitation at 532 nm . [g] Double exponential decay, see text.
substantial difficulty in the preparation of the corresponding coumarin bearing methyl or ethyl substituent at position 6 (see above). The acetal group was not expected to alter the photophysical properties of the coumarin. Cum2 is not fluorescent, most likely because of an intramolecular hydrogen abstraction, which involves the phenolic proton and the nearby carboxylic group. Cum1 and Cum3 display a fluorescence band with a large Stokes-shift ( $\Delta_{\mathrm{ss}}$ ) with respect to the low energy absorption band, $\Delta_{\text {SS }}$ in the order of approximately $6500 \mathrm{~cm}^{-1}$ for both Cum1 and Cum3, which indicates a rather distorted geometry of the excited state. Cum4 exhibits a less shifted emission with respect to the absorption, $\Delta_{\mathrm{SS}}$ in the order of $1200 \mathrm{~cm}^{-1}$. The emission quantum yields (Table 1) range from almost 0 to 0.016 ; this is not surprising because these types of coumarins have been proposed and extensively used as triplet-state sensitizers, because of the large intersystem crossing rate characterizing these compounds. ${ }^{[29]}$ To some extent, our interest in these compounds for the construction of photoactive dyads was based on the characteristic large triplet yield, in the hope to exploit some, rather unusual, triplet energy transfer path.
C3 has been formerly characterized ${ }^{[9 a]}$ and has been shown to be a valuable component of photoactive arrays. ${ }^{[32]}$ In toluene it displays a remarkable luminescence quantum yield, $\Phi_{\mathrm{fl}}=0.14$, upon excitation on the Q and in the Soret bands. Excitation of the dyads in the UV region where both coumarins and corrole absorb in a ratio of almost $50 \%$ (see Figure 1) leads to a complete quenching of the coumarin luminescence ( $\Phi_{\mathrm{fl}}<5 \times 10^{-4}$ ) whereas the corrole luminescence in Cum1-C3, Cum3-C3, and Cum4-C3 is identical within experimental error to that of an optically matched C3 solution, Figure 2. This clearly shows that, irrespective of


Figure 2. Room temperature emission spectra of optically matched toluene solutions of: a) Cum1 (---), C3 (....), Cum1-C3 (-), excitation at $306 \mathrm{~nm}, A=0.17$; b) Cum2 (---, the line is essentially coincident with the zero), C3 (....), Cum2-C3 (full line), excitation at $297 \mathrm{~nm}, A=0.15$; c) Cum3 (---), C3 (…), Cum3-C3 (-), excitation at $341 \mathrm{~nm}, A=0.13$; d) Cum4 (---), C3 (....), Cum4-C3 (-) excitation at $340 \mathrm{~nm}, A=0.11$.
the excited unit, the final recipient of the energy is the corrole component, which indicates an efficient (ca. 100\%) energy transfer process from the coumarin to the corrole.The only exception is Cum2-C3 (Figure 2b) where the fluorescence of the corrole unit is quenched to approximately $9 \%$ of the original emission.

When selective excitation of the corrole moiety at 563 nm is carried on in the dyads (Figure 3), in Cum1-C3 there is again a quenching to $9 \%$, whereas in all the other dyads,


Figure 3. Room temperature emission spectra of optically matched toluene solutions of C3 (.....), Cum1-C3 (-), Cum2-C3 (---), Cum3-C3 $(\Delta)$, Cum4-C3 ( $)$, excitation at $563 \mathrm{~nm}, A=0.12$.
the yield is substantially unaltered with respect to optically matched C3. This indicates that the lowest-lying excited state localized on corrole is photochemically inert in all the dyads except Cum2-C3, where in fact the singlet excited state, $\mathbf{C u m 2}-{ }^{1} \mathbf{C 3}$, reacts as indicated by the decreased fluorescence yield.

Time-resolved luminescence studies with picosecond resolution (Table 1) indicate that the fluorescence lifetimes of the luminescent coumarins is monoexponential for Cum1 and Cum3 with lifetimes of 380 and 230 ps , respectively. Also, no emission from Cum2 could be detected in a timeresolved regime, which is in agreement with the steady-state data. Cum4 displays a luminescence with a biphasic nature: a major component with a lifetime of 50 ps and a minor component with a lifetime of 250 ps . This can be explained by the existence of different conformers non equilibrating during the lifetime of the excited state in Cum4, as already put forward for the interpretation of the phosphorescence spectra in rigid glasses. ${ }^{[29]}$ The lifetime of corrole $\mathbf{C 3}$ in air equilibrated toluene was determined previously and was found to be $3.8 \mathrm{~ns} .{ }^{[9]}$ In the dyads, excitation at 355 nm leads to a very efficient quenching of the coumarin fluorescence lifetime to values below the resolution limit ( $<5 \mathrm{ps}$ ), except in the case of Cum4-C3, where the lifetime of the quenched coumarin unit is 7 ps . The quenching rate constants of the coumarin fluorescence $k_{\mathrm{q}}$, calculated as $k_{\mathrm{q}}=1$ / $\tau-1 / \tau_{0}$ (where $\tau_{0}$ is the lifetime of the model and $\tau$ that of the coumarin in the dyad) are $k_{\mathrm{q}}>2 \times 10^{11} \mathrm{~s}^{-1}$ for Cum1-C3 and Cum3-C3 and $k_{\mathrm{q}}=1.3 \times 10^{11} \mathrm{~s}^{-1}$ for Cum4-C3. It is not possible to derive information on the quenching rate of Cum2-C3 because of the lack of a luminescence signal in the model. Illumination of the dyads at 532 nm leads to selective excitation of corrole; the lifetime of this species is essentially unaltered with respect to the model in all dyads except Cum2-C3, for which a reduction of the corrole lifetime to 470 ps (Figure 4) is measured, in agreement with the quenching detected by steady-state luminescence.


Figure 4. Time evolution of the luminescence registered at 650 nm in toluene after excitation with a laser pulse at $532 \mathrm{~nm}(1.5 \mathrm{~mJ} / \mathrm{pulse})$. Fitting to a mono-exponential lifetime of 440 ps is reported as a gray line for Cum2-C3.

Steady-state and time-resolved data indicate the occurrence of quantitative energy transfer from the coumarin to the corrole for dyads Cum1-C3, Cum3-C3, and Cum4-C3. The rates are extremely fast, but in the case of Cum4-C3, $k_{q}$ could be resolved and measured as $k_{\mathrm{q}}=1.3 \times 10^{11} \mathrm{~s}^{-1}$. Owing to the extended overlap of the donor emission and the acceptor absorption (see Figure 5), an ultrafast energy transfer that occurrs through a Förster mechanism is expected. ${ }^{[33]}$ An


Figure 5. Absorption spectra of the acceptor $\mathbf{C 3}(\cdots \cdots)$ with the luminescence spectra of donor coumarins Cum1 (一), Cum3 (•), and Cum4 ( $\triangle$ ); the emission of coumarins have been scaled proportionally to the luminescence quantum yield.
evaluation of the energy transfer rate according to this mechanism, $k^{F}$ en , can be performed by Equation (1): ${ }^{[33]}$
$k_{e n}^{F}=\frac{8.8 \times 10^{-25} \kappa^{2} \Phi_{f f}}{n^{4} \tau d_{D A}^{6}} J^{F}$
$J^{F}$, the Forster overlap integral calculated from the experimental emission and absorption spectra was found to be $11.2 \times 10^{-14} \mathrm{~cm}^{3} \mathrm{M}^{-1}, \quad 15.5 \times 10^{-14} \mathrm{~cm}^{3} \mathrm{M}^{-1}, \quad$ and $\quad 8.2 \times$ $10^{-14} \mathrm{~cm}^{3} \mathrm{M}^{-1}$ for the system Cum1-C3, Cum3-C3, and Cum4-C3, respectively. The theoretical energy transfer rate can be calculated by substituting the parameters in Equation (1), namely the fluorescence quantum yield $\Phi_{\mathrm{fl}}$ and the lifetime $\tau$ of the donor (Table 1), the refraction index of toluene $n$, the donor-acceptor distance $d_{D A}$, and the orientation factor $\kappa^{2}$ taken as $2 / 3$. The donor-acceptor distance is taken as the center to center distance in the minimized configuration of the dyads, which turns out to be $7.1 \AA$ for $\mathbf{C u m 1 - C 3}$, $7.3 \AA$ for Cum3-C3, and $16.5 \AA$ for Cum4-C3. The calculated $k^{F}$ en $2 \times 10^{12} \mathrm{~s}^{-1}$ for Cum1-C3, $5 \times 10^{12} \mathrm{~s}^{-1}$ for Cum3-C3, and $1.5 \times 10^{11} \mathrm{~s}^{-1}$ for Cum4-C3. The agreement with experimental values, $k_{\mathrm{q}}>2 \times 10^{11} \mathrm{~s}^{-1}$ for Cum1-C3 and Cum3-C3 and $k_{\mathrm{q}}=$ $1.3 \times 10^{11} \mathrm{~s}^{-1}$ for Cum4-C3, is excellent in these dyads, which confirms the interpretation that an energy transfer in agreement with a dipole-dipole mechanism is operative from coumarins to corrole. In the case of dyad Cum2-C3, the nonemissive nature of the excited state seems to indicate that an energy transfer by a Förster mechanism from coumarin to corrole can be excluded; however, occurrence of energy transfer through an exchange mechanism (Dexter mechanism) ${ }^{[34]}$ could be possible.

This would constitute a double electron exchange between the partners in close contact (center to center distance ca. $7.2 \AA$ ) and might be highly competitive with the intrinsic deactivation of the donor. However, experimental evidences indicate that in Cum2-C3 the emission of the corrole unit is not sensitized upon excitation into the coumarins band but it is quenched to $9 \%$. The same quenching ratio is also achieved after direct excitation of the corrole unit. Quite obviously in this dyad, in addition to a possible
energy transfer from the coumarin component to the corrole, a further process depletes the singlet excited state, Cum2- ${ }^{1} \mathbf{C 3}$, localized on corrole.

A schematic energy level diagram of the dyads is shown in Figure 6. The singlet excited state energy levels have been derived from the average of the frequencies of the lon-


Figure 6. Energy level diagram with main deactivation paths and reaction rates in the dyads.
gest wavelength absorption maxima and the shortest wavelength emission maxima at room temperature, which are 1.91 eV for $\mathbf{C 3}, 3.35 \mathrm{eV}$ for $\mathbf{C u m 1}, 3.22 \mathrm{eV}$ for $\mathbf{C u m 3}$, and 2.78 eV for Cum4. For Cum2 which displays no emission, a value of 3.3 eV has been assumed. The data follow the same trend as the energy gap evaluated by cyclic voltammetry in the case of Cum3 $(2.86 \mathrm{eV})$ and Cum4 $(2.50 \mathrm{eV})$, which have both oxidation and reduction in the stability window of the supporting electrolyte (see below). The coumarin triplet excited states are literature values derived from phosphorescence at 77 K and range from 2.2 to $2.3 \mathrm{eV} .{ }^{[32]}$
From Figure 6, it is evident that the quenching of the excited state of corrole in Cum2-C3 can hardly be explained on the basis of any energy transfer process. The fact that the corrole luminescence is quenched to the same extent ( $9 \%$ ) upon excitation of both coumarin and corrole bands in the UV region (Figure 2b) and by selective excitation of corrole at 563 nm (Figure 3), seems to indicate that the process responsible for the quenching is the same. Therefore, it would involve the corrole excited state and not the coumarin excited state, which is not formed when selective excitation of corrole is performed. This is consistent with a $100 \%$ efficient energy transfer process from the coumarin unit to cor-
role in Cum2-C3, similar to what occurs in other dyads. In this case, an electron exchange mechanism (Dexter mechanism) would be operative, as discussed above. Once the excited state $\mathbf{C u m 2}{ }^{1} \mathbf{C} \mathbf{C}$ is formed, a quenching process occurs. In the absence of any reasonable alternative (see Figure 6) this might be identified as an intra-molecular electron transfer from the LUMO of the corrole to the LUMO of the coumarin, which leads to the charge separated (CS) state Cum2 $\mathbf{- C 3}^{+}$. In fact, $\mathbf{C 3}$ can be considered as a moderately good reductant, having an oxidation potential around 0.8 V versus SCE in benzonitrile. ${ }^{[7]}$ On the other hand, the reduction (irreversible) waves of the ketocoumarins in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ have the following half-wave potentials versus SCE: -1.30 V for Cum1; -1.06 V for $\mathbf{C u m 2} ;-1.24 \mathrm{~V}$ for Cum3, and -1.37 V for Cum4. For Cum3 and Cum4, the oxidation wave was also detectable and the half-wave potentials were 1.62 V (irreversible) and 1.13 V (reversible) versus SCE, respectively. It is evident that $\mathbf{C u m} 2$ can be reduced at an energy $0.2-0.3 \mathrm{eV}$ lower than all other coumarins, and as a consequence, the charge separated state level corresponding to $\mathbf{C u m 2} \mathbf{2}^{-}-\mathbf{C 3}^{+}$at sufficiently low energy is present only in Cum2-C3 and not in the other dyads.

An approximate value of the CS state energy level in toluene of 1.9 eV can be calculated if we take into account that in apolar solvents, the classical correction according to Weller overestimates the actual value by ca $0.35 \mathrm{eV} .{ }^{[35]}$ The presence of a low lying charge separated state, $\mathbf{C u m 2}^{-}-\mathbf{C 3}^{+}$, would explain the quenching of the corrole luminescence in this dyad, which can be ascribed to an electron transfer process from the singlet excited state, Cum2- ${ }^{1} \mathbf{C 3}$, localized on the corrole, as depicted in Figure 6. In order to confirm this, experiments to detect transient absorption with picosecond resolution were performed in Cum2-C3 solutions in toluene. The end-of-pulse absorption spectrum in the dyad was compared with the end-of-pulse spectrum in the model $\mathbf{C 3}$ after excitation at 532 nm (only corrole was excited), depicted in Figure 7. The spectral shape of Cum2-C3 has clearly distinct features from that of the model $\mathbf{C 3}$ and may be ascribed to the singlet excited state, ${ }^{1} \mathbf{C} 3{ }^{[92]}$ Differences in the spectra can be detected around $650-700 \mathrm{~nm}$, where the $\mathbf{C} 3$ cation is known to display a broad absorption band. ${ }^{[7]}$ Whereas the spectrum in C3 decays only slightly during the 3.3 ns time


Figure 7. Transient absorbance detected in toluene solutions at the end of a 35 ps pulse ( $532 \mathrm{~nm}, 3 \mathrm{~mJ}$ ), $A=0.65$, of: $\mathbf{C 3}$ (---) and Cum2-C3 (一). The inset shows the time evolution of Cum-C3.
window of the experiment, consistent with a lifetime of 3.8 ns , in Cum2-C3 the band around 680 nm decays with a lifetime of approximately 450 ps (Figure 7). This is essentially coincident with the lifetime of the corrole singlet state, as determined from the time-resolved fluorescence (Table 1). The data, therefore, are supportive of the formation of a charge-separated state, as indicated by the spectral features, but the charge-separated state decays with approximately the same lifetime of the singlet in $\mathbf{C u m} 2{ }^{-1} \mathbf{C 3}$, and it is actually undistinguishable from its formation. This leads us to conclude that the lifetime of the charge separated state is shorter than, or of the order of 450 ps . Given the close spacing of the reduced and oxidized termini of this dyad, this is quite reasonable. No further spectral feature is left after the decay of the species, which indicates a full recovery to the ground state. This is confirmed by laser flash photolysis in the nanosecond range, whereas in the dyads Cum1-C3, Cum3-C3, and Cum4-C3, the triplet state of the corrole is detected, ${ }^{[9]}$ while in Cum2-C3 no absorption could be observed.

## Conclusions

In conclusion, our studies have clearly documented the ability of a $[2+1]$ strategy to assemble meso-linked corrole-coumarin dyads. The target compounds were obtained in a onepot synthesis from dipyrromethanes and formyl-coumarins. The competitive Michael addition of dipyrromethanes to an $\alpha, \beta$-unsaturated system of coumarin most probably diminishes the yield of corroles. The reaction of 2,4-dihydroxybenzaldehyde with vinylphosphonium salts leads to coumarincarboxaldehyde with an unusual substitution pattern. Copper-free Sonogashira coupling can be used for the construction of bis-coumarin-corrole dyads. The spectroscopic properties of all the dyads studied suggest that the components are weakly electronically coupled. Significant Stokes shift and the resulting overlap of coumarin emission with corrole absorption as well as the short spacer between them are responsible for the quantitative and extremely fast energy transfer from the coumarin to the corrole unit, which occurs in most cases by a dipole-dipole mechanism. The excited state of the corrole in the dyads are unreactive with the exception of dyad Cum2-C3 which, as a result of the relatively low reduction potential of coumarin Cum2, displays a low lying charge separated state $\mathbf{C u m 2} \mathbf{2}^{-} \mathbf{C 3}^{+}$, which can be populated by electron transfer. Our data demonstrates that by modulating the electronic properties of coumarins, it is possible to control the processes which take place in cor-role-coumarin dyads.

## Experimental Section

## Synthesis

All chemicals were used as received unless otherwise noted. Reagent grade solvents ( $\mathrm{MeCN}, \mathrm{CH}_{2} \mathrm{Cl}_{2}$, hexane, toluene) were distilled prior to
use. All reported NMR spectra were recorded on a 400 MHz or 500 MHz spectrometer unless otherwise noted. Chemical shifts ( $\delta \mathrm{ppm}$ ) were determined with TMS as the internal reference; $J$ values are given in Hz . UV/Vis absorption spectra were recorded in THF. Chromatography was performed on silica (Kieselgel 60, 200-400 mesh) and dry column vacuum chromatography (DCVC) was performed on preparative thin layer chromatography silica (Merck 107747). Preparative scale size exclusion chromatography (SEC) was performed using BioRad Bio-Beads SX1 with THF as eluent. Mass spectra were obtained by EI or electrospray MS. The following compounds were prepared as described in the literature: $\mathbf{3},{ }^{[36]} \mathbf{8},{ }^{[24]}$ Cum1, ${ }^{[31]}$ and Cum4. ${ }^{[29]}$
6-Formyl-8-methoxy-3-methoxycarbonyl-2-oxo-2 $\boldsymbol{H}$-chromen (4). To a stirred solution of aldehyde $\mathbf{2}(900 \mathrm{mg}, 5 \mathrm{mmol})$ and dimethyl malonate ( $570 \mu \mathrm{~L}, 5 \mathrm{mmol}$ ) in hot $\mathrm{MeOH}(10 \mathrm{~mL})$, pyrrolidine was added ( 5 drops) and the resulting mixture was refluxed for 5 h . Subsequently, the reaction mixture was cooled down to $-17^{\circ} \mathrm{C}$, the precipitate filtered off and washed with cold MeOH to afford $852 \mathrm{mg}(65 \%)$ of coumarin 4 contaminated with a small amount of unidentified impurity of very similar polarity. Every purification attempt failed, and so the crude material was used in the next step. LRMS (EI): $m / z$ (\%) calcd for $\mathrm{C}_{13} \mathrm{H}_{10} \mathrm{O}_{6}: 262\left[M^{+}\right]$; found: 262.
10-(8-Methoxy-3-methoxycarbonyl-2-oxo-2 H-chromen-6-yl)-5,15-bis(pentafluorophenyl)corrole (Cum1-C3). 5-(Pentafluorophenyl)dipyrromethane $\mathbf{3}(125 \mathrm{mg}, 0.4 \mathrm{mmol})$ and coumarin 4 (crude, $52.4 \mathrm{mg}, \sim 0.2 \mathrm{mmol})$ were dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \mathrm{~mL})$. TFA $(10 \mu \mathrm{~L}, 0.13 \mathrm{mmol})$ was added and the reaction mixture was stirred at RT for 1 h . Subsequently, $\mathrm{Et}_{3} \mathrm{~N}$ ( $18 \mu \mathrm{~L}, 0.13 \mathrm{mmol}$ ) was added and the resulting solution was diluted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to 312 mL . DDQ ( $118 \mathrm{mg}, 0.52 \mathrm{mmol}$ ) dissolved in toluene $(1 \mathrm{~mL})$ was added in one portion and stirring was continued for 15 min . The resulting suspension was concentrated and filtered through a short ( 5 cm ) silica pad $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$. Fractions containing the desired product were concentrated and rechromatographed (DCVC, $\mathrm{SiO}_{2}, \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ). Crystallization from $\mathrm{CHCl}_{3} /$ hexanes gave $26 \mathrm{mg}(15 \%)$ of the corrole Cum1-C3. $R_{\mathrm{f}}=0.39\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} /\right.$ acetone $\left.=98: 2\right)$; UV/Vis (toluene): $\lambda=307,417,568$, $615,642 \mathrm{~nm} ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}$, TMS): $\delta=(-3)-(-1)$ (brs, 3 H ), $3.94\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CO}_{2} \mathrm{CH}_{3}\right), 4.10\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 7.98(\mathrm{~d}, J=1.7 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{Ar}), 8.05(\mathrm{~d}, J=1.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 8.60-8.70(\mathrm{~m}, 5 \mathrm{H}, \beta-\mathrm{H}+\mathrm{CH}), 8.77$ $(\mathrm{d}, J=4.6 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H}), 9.17 \mathrm{ppm}(\mathrm{d}, J=4.4 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H}) ;$ HRMS (ESI): m/z (\%) calcd for $\mathrm{C}_{43} \mathrm{H}_{21} \mathrm{~F}_{10} \mathrm{~N}_{4} \mathrm{O}_{5}: 863.1347\left[M+\mathrm{H}^{+}\right]$; found: 863.1378; elemental analysis: calcd (\%) for $\mathrm{C}_{43} \mathrm{H}_{21} \mathrm{~F}_{10} \mathrm{~N}_{4} \mathrm{O}_{5}$ : C 59.87, H 2.34, N 6.49; found: C 59.94, H 2.37, N 6.31 .
6-Formyl-5-hydroxy-4-metoxycarbonyl-2-oxo-2 $\boldsymbol{H}$-chromen (6). 2,4-Dihydroxybenzaldehyde $(5,5.56 \mathrm{~g}, 40 \mathrm{mmol})$ and $\mathrm{PPh}_{3}(10.6 \mathrm{~g}, 40 \mathrm{mmol})$ were dissolved in anhydrous toluene ( 100 mL ). The reaction mixture was cooled down to $-5^{\circ} \mathrm{C}$ and dimethyl acetylenedicarboxylate $(4.94 \mathrm{~mL}$, 40 mmol ) in anhydrous toluene ( 50 mL ) was slowly ( 5 min ) added. The resulting mixture was refluxed for 8 h under the argon atmosphere, then the solvent was removed and the residue was refluxed with MeOH. Crystalls were filtered off and washed with cold MeOH to afford 3.64 g of 6 ( $37 \%$ ). M.p.: $219-221^{\circ} \mathrm{C}$; IR ( KBr ): $\tilde{v}=819,1019,1268,1650,1743$, $3085 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz},\left[\mathrm{D}_{6}\right]$ DMSO, $25^{\circ} \mathrm{C}, \mathrm{TMS}$ ): $\delta=3.89(\mathrm{~s}, 3 \mathrm{H}$, $\mathrm{CO}_{2} \mathrm{CH}_{3}$ ), $6.67(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}), 7.12(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 8.02(\mathrm{~d}, J=$ $8.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 10.03(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CHO}), 12.30 \mathrm{ppm}$ (brs, $1 \mathrm{H}, \mathrm{OH}$ ); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz},\left[\mathrm{D}_{6}\right] \mathrm{DMSO}, 25^{\circ} \mathrm{C}$, TMS): $\delta=53.0,105.8,109.4$, 113.5, 117.8, 136.2, 143.9, 157.9, 158.4, 158.9, 165.6, 194.5 ppm ; HRMS (EI): $m / z$ (\%) calcd for $\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{O}_{6}: 248.0321$ [ $M^{+}$]; found: 248.0331; elemental analysis: calcd (\%) for $\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{O}_{6}$ : C 58.07, H 3.25; found: C 57.97, H3.25.
Methyl 6-(5,5-dimethyl-1,3-dioxan-2-yl)-5-hydroxy-2-oxo-2 H -chromene-4-carboxylate (Cum2). A solution of coumarin $\mathbf{6}$ ( $300 \mathrm{mg}, 1.2 \mathrm{mmol}$ ), 2,2-dimethylpropane-1,3-diol and $\mathrm{TsOH} \cdot \mathrm{H}_{2} \mathrm{O}(23 \mathrm{mg}, 0.12 \mathrm{mmol})$ in toluene $(50 \mathrm{~mL})$ was refluxed with Dean-Stark apparatus for 2.5 h . The solvent was removed under reduced pressure and the residue was purified by column chromatography using dichloromethane and dichloromethane/ ethyl acetate (98:2). The product was recrystallized from chloroform/ hexane (1:1) to give coumarin Cum2 as white crystals ( $236 \mathrm{mg}, 58 \%$ ). $R_{\mathrm{f}}=0.5$ (hexane/ethyl acetate $=1: 1$ ); m.p.: $165^{\circ} \mathrm{C}$; UV/Vis (chloroform): $\lambda\left(\varepsilon \times 10^{-2} / \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~cm}^{-1}\right) 301$ (114); ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}$,

TMS): $\delta=9.15(\mathrm{~s}, 1 \mathrm{H}, \mathrm{OH}), 7.40(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 6.88$ (d, $J=$ $8.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 6.28(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}=), 5.59(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}), 3.95(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{OCH}_{3}\right), 3.83\left(\mathrm{~d}, J=11.4 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.69\left(\mathrm{~d}, J=11.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$, $1.27\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 0.84 \mathrm{ppm}\left(\mathrm{s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$, $25^{\circ} \mathrm{C}$, TMS): $\delta=166.8,159.6,155.4,152.3,144.9,131.8,117.7,113.1$, 108.5, 105.9, 102.0, 76.7, 53.1, 30.4, 22.9, 21.7 ppm; HR ESI-MS: m/z (\%) calcd. for $\left[\mathrm{C}_{17} \mathrm{H}_{18} \mathrm{O}_{7} \mathrm{Na}\right.$ ]: 357.0945; found: 357.0932 ; elemental analysis: calcd (\%) for $\mathrm{C}_{17} \mathrm{H}_{18} \mathrm{O}_{7}$ : C 61.07, H 5.43; found C 61.11, H 5.56.

10-(5-Hydroxy-4-methoxycarbonyl-2-oxo-2 H -chromen-6-yl)-5,15-bis(pentafluorophenyl)corrole (Cum2-C3). 5-(Pentafluorophenyl)dipyrromethane (3) ( $1.25 \mathrm{~g}, 4 \mathrm{mmol}$ ) and coumarin $\mathbf{6}(496 \mathrm{mg}, 2 \mathrm{mmol})$ were dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(30 \mathrm{~mL})$. TFA ( $100 \mu \mathrm{~L}, 1.32 \mathrm{mmol}$ ) was added and the resulting mixture was stirred at RT for 1 h . Then $\mathrm{Et}_{3} \mathrm{~N}(181 \mu \mathrm{~L}$, 0.04 mmol ) was added, followed by $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$. DDQ ( 1.18 g , $5.2 \mathrm{mmol})$ was dissolved in a toluene $/ \mathrm{CH}_{2} \mathrm{Cl}_{2}(1: 1,40 \mathrm{~mL})$ mixture and both solutions were added simultaneously to $\mathrm{CH}_{2} \mathrm{Cl}_{2}(50 \mathrm{~mL})$ with vigorous stirring. After 15 mins , the reaction mixture was concentrated to a quarter of the initial volume and filtered through a short $(5 \mathrm{~cm})$ silica pad $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$. The fluorescent band was collected, evaporated, and rechromatographed ( $\mathrm{DCVC}, \mathrm{SiO}_{2}, \mathrm{CH}_{2} \mathrm{Cl}_{2} /$ hexane $=3: 2$, then $4: 1, \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ). Crystallization from $\mathrm{CHCl}_{3} /$ hexane gave $101 \mathrm{mg}(6 \%)$ of the corrole Cum2-C3. $R_{\mathrm{f}}=0.43\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ /acetone $\left.=98: 2\right)$; UV/Vis (toluene): $\lambda=424$, $565,611,640 \mathrm{~nm} ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}$, TMS): $\delta=(-3)-$ $(-1)($ brs, 3 H$), 3.75\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CO}_{2} \mathrm{CH}_{3}\right), 6.55(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}), 7.30(\mathrm{~d}, J=$ $8.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 8.11$ (d, $J=8.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 8.59(\mathrm{~d}, 2 \mathrm{H}, J=4.2 \mathrm{~Hz}, \beta-$ H), $8.62(\mathrm{~d}, J=4.7 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H}), 8.75(\mathrm{~d}, J=4.7 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H}), 9.14 \mathrm{ppm}$ (d, $J=4.2 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H}$ ), signal from OH could not be identified; LRMS (EI): $m / z$ (\%) calcd for $\mathrm{C}_{42} \mathrm{H}_{18} \mathrm{~F}_{10} \mathrm{~N}_{4} \mathrm{O}_{5}: 848.1$ [ $\left.M^{+}\right]$; found: 848.0; elemental analysis: calcd (\%) for $\mathrm{C}_{42} \mathrm{H}_{18} \mathrm{~F}_{10} \mathrm{~N}_{4} \mathrm{O}_{5}$ : C 59.44, H 2.14, N 6.60; found: C 59.64, H 2.33, N 6.57 .
6-Formyl-7-hydroxy-4-methoxycarbonyl-8-methyl-2-oxo-2 H-chromen (9). This compound was prepared exactly according to the procedure described for $\mathbf{6}$. Starting from aldehyde $\mathbf{8}(1.52 \mathrm{~g}, 10 \mathrm{mmol}), 1.53 \mathrm{~g}(59 \%)$ of the product was obtained. M.p.: $165-167^{\circ} \mathrm{C}$; IR ( KBr ): $\tilde{v} 757,1148,1580$, 1617, 1658, 1722, 1751, 1806, $3080 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz},\left[\mathrm{D}_{6}\right] \mathrm{DMSO}\right.$, $25^{\circ} \mathrm{C}$, TMS): $\delta=2.22\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 3.96\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CO}_{2} \mathrm{CH}_{3}\right), 6.80(\mathrm{~s}, 1 \mathrm{H}$, CH ), 8.42 ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{Ar}$ ), 10.13 ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{CHO}$ ), $11.56 \mathrm{ppm}(\mathrm{brs}, 1 \mathrm{H}, \mathrm{OH})$; ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz},\left[\mathrm{D}_{6}\right] \mathrm{DMSO}, 25^{\circ} \mathrm{C}, \mathrm{TMS}$ ): $\delta=7.7,53.3,108.7,113.2$, 115.8, 118.5, 129.7, 142.3, 156.7, 158.9, 161.2, 164.0, 195.4 ppm. HRMS (EI): $m / z$ (\%) calcd for $\mathrm{C}_{13} \mathrm{H}_{10} \mathrm{O}_{6}: 262.0477$ [ $M^{+}$]; found: 262.0468; elemental analysis: calcd (\%) for $\mathrm{C}_{13} \mathrm{H}_{10} \mathrm{O}_{6}$ : C 59.55, H 3.84; found: C 59.65, H 3.79.

## 10-(7-Hydroxy-4-methoxycarbonyl-8-methyl-2-oxo-2 H-chromen-6-yl)-

 5,15-bis(pentafluorophenyl)corrole (Cum3-C3). This compound was prepared exactly according to the procedure described for Cum2-C3. Starting from 5-(pentafluorophenyl)dipyrromethane ( $1.25 \mathrm{~g}, 4 \mathrm{mmol}$ ) and coumarin 9 ( $524 \mathrm{mg}, 2 \mathrm{mmol}$ ), 46 mg ( $3 \%$ ) of the corrole Cum3-C3 was obtained. $R_{\mathrm{f}}=0.54\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} /\right.$ acetone $\left.=98: 2\right)$; UV/Vis (toluene): $\lambda=423,564$, $609,634 \mathrm{~nm} ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}$, TMS): $\delta=(-3)-(-1)$ (brs, 3 H ), $2.59\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 3.78\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CO}_{2} \mathrm{CH}_{3}\right), 6.89(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH})$, $8.55-8.70(\mathrm{~m}, 5 \mathrm{H}, \mathrm{Ar}+\beta-\mathrm{H}), 8.76(\mathrm{~m}, 2 \mathrm{H}, \beta-\mathrm{H}), 9.14 \mathrm{ppm}(\mathrm{m}, 2 \mathrm{H}, \beta-\mathrm{H})$, signal from OH couldn't be identified; HRMS (EI): m/z (\%) calcd for $\mathrm{C}_{43} \mathrm{H}_{20} \mathrm{~F}_{10} \mathrm{~N}_{4} \mathrm{O}_{5}$ : $862.1274\left[M^{+}\right]$; found: 862.1297.Methyl 7-hydroxy-8-methyl-2-oxo-2 H-chromene-4-carboxylate (Cum3). A solution of DMAD ( $615 \mu \mathrm{~L}, 5 \mathrm{mmol}$ ) in dry toluene ( 2 mL ) was added dropwise for 15 min to a cooled $\left(-5^{\circ} \mathrm{C}\right)$ solution of 2-methylresorcinol $(7,620 \mathrm{mg}, 5 \mathrm{mmol})$ and triphenylphosphine $(1.310 \mathrm{~g}, 5 \mathrm{mmol})$ in dry toluene $(15 \mathrm{~mL})$. The reaction mixture was then refluxed for 8 h . The solvent was removed under reduced pressure and the residue was purified by column chromatography using toluene/ethyl acetate, changing concentration of ethyl acetate from $0 \%$ to $20 \%$. The product was recrystallized from chloroform with the addition of a small amount of methanol to give coumarin Cum3 as yellowish crystals ( $241 \mathrm{mg}, 20 \%$ ). $R_{\mathrm{f}}=0.3$ (toluene/ ethyl acetate $=7: 3$ ); m.p.: $202^{\circ} \mathrm{C}$; UV/Vis (THF): $\lambda \quad\left(\varepsilon \times 10^{-2} /\right.$ $\mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~cm}^{-1}$ ) 347 (107) nm; ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz},\left[\mathrm{D}_{6}\right] \mathrm{DMSO}, 25^{\circ} \mathrm{C}$, TMS): $\delta=10.64(\mathrm{~s}, 1 \mathrm{H}, \mathrm{OH}), 7.73$ (d, $J=8.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 6.89$ (d, $J=$ $8.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 6.56(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}=), 3.92\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 2.17 \mathrm{ppm}(\mathrm{s}$, $3 \mathrm{H}, \mathrm{CH}_{3}$ ) ; ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz},\left[\mathrm{D}_{6}\right] \mathrm{DMSO}, 25^{\circ} \mathrm{C}, \mathrm{TMS}$ ): $\delta=164.5$,
$159.8,159.5,153.6,143.5,124.5,112.7,112.3,111.2,107.6,53.0,7.9 \mathrm{ppm} ;$ HR EI-MS: $m / z$ (\%) calcd. for $\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{O}_{5}$ : 234.0528; found: 234.0520; elemental analysis: calcd (\%) for $\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{O}_{5}$ : C 61.54, H 4.30; found C 61.52, H 4.40.

10-[4-(2'-Trimethylosilylethyn-1-ylo)phenyl]-5,15-bis(pentafluorophenyl)corrole. To a stirred solution of 5-(pentafluorophenyl)dipyrromethane ( $\mathbf{3}$ $1.56 \mathrm{~g}, 5.0 \mathrm{mmol})$ and aldehyde $10(505 \mathrm{mg}, 2.5 \mathrm{mmol})$ in MeOH ( 250 mL ), aqueous $\mathrm{HCl}(36 \%, 12.5 \mathrm{~mL})$ in $\mathrm{H}_{2} \mathrm{O}(250 \mathrm{~mL})$ was added and the resulting suspension was stirred at RT for 1 h . The reaction mixture was then extracted with $\mathrm{CHCl}_{3}(2 \times 50 \mathrm{~mL})$, and the organic phases were washed with water $(2 \times 50 \mathrm{~mL})$ and dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$. The drying agent was removed and the mixture was concentrated to 60 mL . DDQ ( 1.47 g , $6.5 \mathrm{mmol})$ was dissolved in toluene $/ \mathrm{CH}_{2} \mathrm{Cl}_{2}(1: 1,60 \mathrm{~mL})$ mixture and both solutions were added simultaneously to $\mathrm{CH}_{2} \mathrm{Cl}_{2}(50 \mathrm{~mL})$ with vigorous stirring. After 15 min . the reaction mixture was concentrated to a quarter of the initial volume and filtered through a short $(5 \mathrm{~cm})$ silica pad $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} /\right.$ hexane $\left.=1: 1\right)$. The fluorescent band was collected, evaporated and rechromatographed ( $\mathrm{DCVC}, \mathrm{SiO}_{2}, \mathrm{CH}_{2} \mathrm{Cl}_{2} /$ hexane $=1: 4$ ). Crystallization from hexane gave $475 \mathrm{mg}(24 \%)$ of product. $R_{\mathrm{f}}=0.62\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ hexane $=2: 3$ ); UV/Vis (toluene): $\lambda\left(\varepsilon \times 10^{-3}\right) 424$ (106), 564 (16.8), 615 (9.8), 641 (6.67) nm; ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}$, TMS): $\delta=(-4)-$ $(-1.5)$ (br s $, 3 \mathrm{H}, \mathrm{NH}$ ), 0.37 (s, $9 \mathrm{H}, 3 \times \mathrm{CH}_{3}$ ), 7.87, 8.11 ( $\mathrm{AA}^{\prime} \mathrm{BB}^{\prime}, J=$ $\left.8.1 \mathrm{~Hz}, 2 \times 2 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{4}\right), 8.55(\mathrm{br} \mathrm{d}, J=3.6 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H}), 8.66(\mathrm{~d}, J=4.6 \mathrm{~Hz}$, $2 \mathrm{H}, \beta-\mathrm{H}), 8.71$ (d, $J=4.6 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H}), 9.08 \mathrm{ppm}(\mathrm{d}, J=4.2 \mathrm{~Hz}, 2 \mathrm{H}, \beta-$ H ); LRMS (EI): $m / z(\%)$ calcd for $\mathrm{C}_{42} \mathrm{H}_{24} \mathrm{~F}_{10} \mathrm{~N}_{4} \mathrm{Si}: 802.2$ [ $\left.M^{+}\right]$; found: 802; elemental analysis: calcd (\%) for $\mathrm{C}_{42} \mathrm{H}_{24} \mathrm{~F}_{10} \mathrm{~N}_{4} \mathrm{Si}$ : C 62.84, H 3.01, N 6.98; found: C 62.79, H 2.95, N 6.93 .

10-(4-Ethynylphenyl)-5,15-bis(pentafluorophenyl)corrole (11). To a stirred solution of 10-[4-(2'-trimethylosilylethyn-1-ylo)phenyl]-5,15-bis(pentafluorophenyl)corrole ( $60 \mathrm{mg}, 75 \mu \mathrm{~mol}$ ) in $\mathrm{CHCl}_{3}(3 \mathrm{~mL}$ ) TBAF ( 1 m solution in THF, $150 \mu \mathrm{~L}, 150 \mu \mathrm{~mol}$ ) was added. The resulting mixture was stirred at RT for 2 h . The solvent was removed under reduced pressure and the residue was chromatographed $\left(\mathrm{DCVC}, \mathrm{SiO}_{2}, \mathrm{CH}_{2} \mathrm{Cl}_{2} /\right.$ hexane $=$ $2: 3$, then $1: 1$ ). Crystallization from hexane gave $50 \mathrm{mg}(91 \%)$ of the corrole 11. $R_{\mathrm{f}}=0.52\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} /\right.$ hexane $\left.=2: 3\right)$; UV/Vis (toluene): $\lambda=\left(\varepsilon \times 10^{-3}\right)$ 421 (103), 564 (15.9), 615 (9.4), 641 (6.29) nm; ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}, \mathrm{TMS}\right): \delta=(-4)-(-1.5)(\mathrm{brs}, 3 \mathrm{H}, \mathrm{NH}), 3.30(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH})$, $7.89,8.14\left(\mathrm{AA}^{\prime} \mathrm{BB}^{\prime}, J=8.0 \mathrm{~Hz}, 2 \times 2 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{4}\right.$ ), 8.56 (br d, $J=3.3 \mathrm{~Hz}, 2 \mathrm{H}$, $\beta-\mathrm{H}), 8.67(\mathrm{~d}, J=4.7 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H}), 8.71(\mathrm{~d}, J=4.7 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H})$, $9.10 \mathrm{ppm}(\mathrm{d}, J=4.2 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H})$; HRMS (EI): m/z (\%) calcd for $\mathrm{C}_{39} \mathrm{H}_{16} \mathrm{~F}_{10} \mathrm{~N}_{4}$ : $730.1215\left[M^{+}\right]$; found: 730.1204.
6-Bromo-7-diethylamino-3-[(7-diethylamino-2-oxo-2 H-chromen-3-yl)car-bonyl]-4a,8 a-dihydro-2 H -chromen-2-on (14). To a stirred solution of aldehyde $12(417 \mathrm{mg}, 1.54 \mathrm{mmol})$ and ester $\mathbf{1 3}(488 \mathrm{mg}, 1.54 \mathrm{mmol})$ in hot $\mathrm{MeOH}(60 \mathrm{~mL})$, pyrrolidine ( $80 \mu \mathrm{~L}, 0.96 \mathrm{mmol}$ ) was added, followed by $\mathrm{AcOH}(60 \mu \mathrm{~L}, 0.96 \mathrm{mmol})$ and the reaction mixture was refluxed for 6 h The resulting mixture was cooled down, the precipitate filtered off and washed with cold MeOH to afford 689 mg ( $83 \%$ ) of the coumarin 14 M.p.: $222-223^{\circ} \mathrm{C}$; UV/Vis (toluene): $\lambda=445 \mathrm{~nm}$; IR (KBr): 1133, 1190, 1198, 1351, 1508, 1589, 1617, $1721 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$, $25^{\circ} \mathrm{C}$, TMS): $\delta=1.13\left(\mathrm{t}, J=7.0 \mathrm{~Hz}, 6 \mathrm{H}, 2 \times \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.24(\mathrm{t}, J=7.1 \mathrm{~Hz}$, $\left.6 \mathrm{H}, 2 \times \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 3.28\left(\mathrm{q}, J=7.0 \mathrm{~Hz}, 4 \mathrm{H}, 2 \times \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 3.46(\mathrm{q}, J=$ $7.1 \mathrm{~Hz}, 4 \mathrm{H}, 2 \times \mathrm{CH}_{2} \mathrm{CH}_{3}$ ), $6.48(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 6.62\left(\mathrm{dd},{ }^{3} J=\right.$ $\left.9.0 \mathrm{~Hz},{ }^{4} J=2.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}\right), 6.94(\mathrm{~s}, 1 \mathrm{H}, \mathrm{Ar}), 7.41(\mathrm{~d}, J=9.0 \mathrm{~Hz}, 1 \mathrm{H}$, Ar), 7.75 (s, 1H, Ar), 7.99 (s, 1H, CH), $8.29 \mathrm{ppm}(\mathrm{s}, 1 \mathrm{H}, \mathrm{CH}),{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}, \mathrm{TMS}$ ): $\delta=12.2,12.4,45.1,45.2,97.1,108.5$, 109.7, 109.8, 114.2, 114.4, 118.3, 126.6, 131.6, 133.9, 142.5, 146.9, 152.9, 154.1, 154.9, 158.5, 159.1, 160.5, 187.9 ppm. HRMS (EI): $m / z$ (\%) calcd for $\mathrm{C}_{27} \mathrm{H}_{27} \mathrm{~N}_{2} \mathrm{O}_{5} \mathrm{Br}$ : $538.1103\left[\mathrm{M}^{+}\right]$; found: 538.1123 .

Corrole Cum4-C3. Corrole 11 ( $144 \mathrm{mg}, 198 \mu \mathrm{~mol}$ ), coumarin 14 ( 130 mg , $240 \mu \mathrm{~mol}), \mathrm{Cs}_{2} \mathrm{CO}_{3}(69 \mathrm{mg}, 210 \mu \mathrm{~mol}), \mathrm{Pd}(\mathrm{OAc})_{2}(11.0 \mathrm{mg}, 50 \mu \mathrm{~mol})$ and $\mathrm{PPh}_{3}(51 \mathrm{mg}, 198 \mu \mathrm{~mol})$ were placed under an Ar atmosphere in a dry Schlenk flask. DMSO (dry, saturated with Ar, 2 mL ) was added and the whole reaction mixture was stirred at $80^{\circ} \mathrm{C}$ for 24 h . The solvent was removed under reduced pressure and the residue was chromatographed $\left(\mathrm{SiO}_{2}, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$, then $\mathrm{CH}_{2} \mathrm{Cl}_{2} /$ acetone $\left.=98: 2\right)$. Fractions containing the desired product were collected, evaporated and rechromatographed (SEC, THF). Crystallization from $\mathrm{CHCl}_{3} /$ hexane gave $70 \mathrm{mg}(30 \%)$ of the cor-
role Cum4-C3. $R_{\mathrm{f}}=0.62\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ /acetone $\left.=95: 5\right)$; UV/Vis (toluene): $\lambda=$ 435, 566, 616, 640 nm ; ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}$, TMS): $\delta=$ $(-4)-(-1.5)($ brs, $3 H, N H), 1.25\left(\mathrm{t}, J=7.1 \mathrm{~Hz}, 6 \mathrm{H}, 2 \times \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.40(\mathrm{t}$, $\left.J=7.1 \mathrm{~Hz}, 6 \mathrm{H}, 2 \times \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 3.46\left(\mathrm{q}, 7.1 \mathrm{~Hz}, 4 \mathrm{H}, 2 \times \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 3.80(\mathrm{q}$, $\left.J=7.1 \mathrm{~Hz}, 4 \mathrm{H}, 2 \times \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 6.62(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 6.72(\mathrm{~s}, 1 \mathrm{H}$, Ar), 6.85 (dd, $\left.{ }^{3} J=9.0 \mathrm{~Hz},{ }^{4} J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}\right), 7.69(\mathrm{~d}, J=9.0 \mathrm{~Hz}, 1 \mathrm{H}$, Ar), $7.79(\mathrm{~s}, 1 \mathrm{H}, \mathrm{Ar}), 8.00,8.25\left(\mathrm{AA}^{\prime} \mathrm{BB}^{\prime}, J=7.9 \mathrm{~Hz}, 2 \times 2 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{4}\right), 8.35$ (s, $1 \mathrm{H}, \mathrm{Ar}$ ), 8.47 (s, $1 \mathrm{H}, \mathrm{CH}$ ), 8.60 (brs, $2 \mathrm{H}, \beta-\mathrm{H}$ ), 8.76 (br s, $4 \mathrm{H}, \beta-\mathrm{H}$ ), 9.10 (br d, $J=3.2 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H}$ ). LRMS (FD): $m / z$ (\%) calcd for $\mathrm{C}_{66} \mathrm{H}_{42} \mathrm{~F}_{10} \mathrm{~N}_{6} \mathrm{O}_{5}$ : $1188.3\left[M^{+}\right]$; found: 1188.3; elemental analysis: calcd (\%) for $\mathrm{C}_{66} \mathrm{H}_{42} \mathrm{~F}_{10} \mathrm{~N}_{6} \mathrm{O}_{5}$ : C 66.67, H 3.56, N 7.07; found: C 66.48, H 3.64, N 7.07.

## Spectroscopy and Photophysics

Spectrophotometric grade toluene (C. Erba) was used as supplied. A Perkin-Elmer Lambda 950 UV/Vis spectrophotometer was used to measure absorption spectra in 10 mm pathlength cells. Molar absorption coefficient of coumarins were measured in toluene with $5 \%$ spectrophotometric grade dichloromethane (C. Erba) in order to allow solubilization. Spex Fluorolog II spectrofluorimeter was used to acquire fluorescence spectra in standard 10 mm pathlength fluorescence cells. The reported luminescence spectra are uncorrected, and emission quantum yields were determined after correction for the photomultiplier response with reference to an air-equilibrated toluene solution of $\mathbf{C} 3$ with a $\Phi_{f l}=0.14 .{ }^{[9]]} \mathrm{Lu}-$ minescence lifetimes in the nanosecond range were obtained with IBH single photon counting equipment. For determination of emission lifetimes in the picosecond range, a set-up involving a Nd:YAG laser (35 ps pulse duration, $532 \mathrm{~nm}, 1.5 \mathrm{~mJ}$ ) and a Streak Camera was used. Solutions with absorbance of ca. 0.5 at the excitation wavelength were irradiated by the laser pulse and light was collected at a right angle. Improvement of the convolution procedure and of the signal to noise ratio of the experiment allowed a progress of the time resolution of the apparatus to approximately 5 ps , compared to the formerly reported $10 \mathrm{ps}{ }^{[37]}$ Transient absorbance in the picosecond range was measured using a pump and probe system based on a Nd-YAG laser (Continuum PY62/10, 35 ps pulse, $532 \mathrm{~nm}, 3.5 \mathrm{~mJ}$ ). Solutions with absorbance of approximately 0.6 at the excitation wavelength were used. More details on the apparatus can be found elsewhere. ${ }^{[38]}$ Laser flash photolysis in the nanosecond range was performed with a Nd-YAG laser ( 18 ns pulse, $532 \mathrm{~nm}, 3 \mathrm{~mJ}$ ) and an apparatus previously described. ${ }^{[39]}$ The samples were bubbled with argon for ca. 15 min and sealed in home made 10 mm optical cells. Molecular dimensions were estimated after MM2 minimization by CS Chem 3D Ultra 6.0 software ${ }^{[40]}$ The parameters used to compute the charge separated state energy by the Weller equation ${ }^{[32 a]}$ in toluene are: $r_{A D}=7.2 \AA$, $\mathrm{r}_{\mathrm{D}}=5 \AA, \mathrm{r}_{\mathrm{A}}=3.5 \AA, \varepsilon_{\mathrm{P}}=17.9$ (the average of dichloromethane and benzonitrile dielectric constants) and $\varepsilon_{S}=2.4$, see Ref. [10b] for more details. Computation of the integral overlap and of the rate for the energy transfer processes according to Förster mechanism were performed with the use of Matlab 5.2. ${ }^{[41]}$ Estimated errors are $10 \%$ on lifetimes for single exponentials, $20 \%$ on more complex kinetics, $20 \%$ on quantum yields, $20 \%$ on molar absorption coefficients and 3 nm on emission and absorption peaks.

## Electrochemistry

Redox potentials have been determined at RT on millimolar coumarin solutions in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ (C. Erba RPE, distilled over $\mathrm{P}_{2} \mathrm{O}_{5}$ and stored under Ar pressure) with $0.1 \mathrm{~m}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4} \mathrm{NClO}_{4}$ (Fluka, puriss. crystallized from $\mathrm{CH}_{3} \mathrm{OH}$ and vacuum dried). After Ar bubbling, cyclic voltammetries were performed at $0.1 \mathrm{Vs}^{-1}$ in a home-made three compartment glass electrochemical cell under Ar pressure, by using an AMEL electrochemical system model 5000. Working electrode was semi-spherical Pt (area $0.05 \mathrm{~cm}^{2}$ ), reference electrode was an aqueous KCl Saturated Calomel Electrode (SCE) and auxiliary electrode was a Pt wire. SCE electrode was separated from the working electrode compartment by a liquid bridge, which contained the same solvent and support electrolyte, and a low porosity glass frit.

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