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Trans-A₂B-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*- A_2B -corroles by reaction with 5-(penta-fluorophenyl)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

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

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E-mail: flamigni@isof.cnr.it 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 dipole– dipole 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 electron-transfer was detected from corrole to coumarin. The latter process is possible because of the suitably low reduction potential of coumarins of this type.

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.

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Results and Discussion

Design and Synthesis

Trans-A2B-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 4 under classical Knoevenagel conditions. This aldehyde was reacted^[21] with dipyrromethane 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 vinyl-phosphonium salts (formed in situ from DMAD and PPh₃) 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 DMAD/PPh₃ under reported

Abstract in Polish: Cztery układy dwuchromoforowe, składające się z jednostek korolowych i kumarynowych zsyntetyzowano poprzez kondensację formylokumaryn z 5-(pentafluorofenylo)dipirometanem. Udowodniono, że reakcja aldehydów hydroksybenzoesowych z solami winylofosfoniowymi jest najbardziej ogólną metodą syntezy formylokumaryn. Badania spektroskopowe i fotofizyczne wykazały istnienie transferu energii od układu kumaryny do pierścienia korolu. Transfer ten zachodzi według mechanizmu Förstera 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.



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 6 was condensed with dipyrromethane 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 $8^{[25]}$ 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**, **Cum2-C3**, and **Cum3-C3** stem from the possible side reactions, especially Michael addition of pyrrole derivatives to the α , β -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 formylketobis-coumarin. Sonogashira reaction was identified as the means to form the link between the chromophores. Ethynyl-corrole **11** was prepared from aldehyde **10**^[26] and dipyrromethane **3** under H₂O/MeOH/HCl conditions^[27] (Scheme 4). The second building block was prepared from aldehyde **12**^[28] and β-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

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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

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 5– 10 nm in the dyads and the 640 nm band is less intense. Though sizeable, the perturbation on the spectroscopic prop-

erties are however modest and

it can be safely assumed that

the components in the dyads

are electronically decoupled in

formyl group as acetal (Scheme 2). Finally, coumarins $Cum1^{[31]}$ and $Cum4^{[29]}$ (Scheme 6) were synthesized using known procedures.

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

(Figure 1d).



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 Cum2 and Cum3 display a single band in the UV region, at 297 nm ($\varepsilon = 10800 \,\mathrm{M}^{-1} \mathrm{cm}^{-1}$) for Cum2 and at 341 nm ($\varepsilon = 9700 \,\mathrm{M}^{-1} \mathrm{cm}^{-1}$) for **Cum3. Cum1** exhibits a band at 306 nm ($\varepsilon = 14200 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at 360 nm ($\varepsilon = 1700 \,\mathrm{M}^{-1} \mathrm{cm}^{-1}$). The absorption band of **Cum4** is at lower energies, $\lambda = 446$ 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 nm ($\varepsilon = 120600 \,\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$) and lower intensity Q bands at 523, 562, 617 and 640 nm $(10\,000\,{\rm M}^{-1}\,{\rm cm}^{-1} < \varepsilon < 20\,000\,{\rm M}^{-1}\,{\rm cm}^{-1})$. 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 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.

all cases.



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 (--).

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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	$\lambda_{\max} [nm]^{[a]}$	$arPsi_{ ext{fl}}{}^{[b]}$	${\pmb{\varPhi}_{\mathrm{fl}}}^{[\mathrm{c}]}$	$arPsi_{ m fl}{}^{[m d]}$	$\tau [\mathrm{ns}]^{[\mathrm{e}]}$	τ [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	-	-	0.05 (75%), ^[g]	-
					0.25 (75%) ^[g]	
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] λ_{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 (Δ_{SS}) with respect to the low energy absorption band, Δ_{SS} in the order of approximately 6500 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, $\Delta_{\rm SS}$ in the order of 1200 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^[9a] and has been shown to be a valuable component of photoactive arrays.^[32] In toluene it displays a remarkable luminescence quantum yield, $\Phi_{\rm fl}$ =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 ($\Phi_{\rm fl} < 5 \times 10^{-4}$) 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 nm, A = 0.17; b) **Cum2** (---, the line is essentially coincident with the zero), **C3** (....), **Cum2-C3** (full line), excitation at 297 nm, A = 0.15; c) **Cum3** (---), **C3** (....), **Cum3-C3** (—), excitation at 341 nm, A = 0.13; d) **Cum4** (---), **C3** (....), **Cum4-C3** (—) excitation at 340 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 (\triangle), Cum4-C3 (\bullet), excitation at 563 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, **Cum2-¹C3**, 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 C3 in air equilibrated toluene was determined previously and was found to be 3.8 ns.^[9a] 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 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_q , calculated as $k_q = 1/$ $\tau {-}1{/}\tau_0$ (where τ_0 is the lifetime of the model and τ that of the coumarin in the dyad) are $k_q > 2 \times 10^{11} \text{ s}^{-1}$ for **Cum1-C3** and **Cum3-C3** and $k_q = 1.3 \times 10^{11} \text{ s}^{-1}$ 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 nm (1.5 mJ/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 $k_q = 1.3 \times 10^{11} \text{ s}^{-1}$. 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 C3 (·····) with the luminescence spectra of donor coumarins Cum1 (—), 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_{en}^{F} , can be performed by Equation (1):^[33]

$$k_{en}^{F} = \frac{8.8 \times 10^{-25} \kappa^{2} \Phi_{fl}}{n^{4} \tau \, d_{DA}^{6}} J^{F} \tag{1}$$

 J^{F} , the Forster overlap integral calculated from the experimental emission and absorption spectra was found to be $11.2 \times 10^{-14} \text{ cm}^3 \text{ M}^{-1}$, $15.5 \times 10^{-14} \text{ cm}^3 \text{ M}^{-1}$, and $8.2 \times$ $10^{-14} \text{ cm}^3 \text{M}^{-1}$ 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 $\Phi_{\rm fl}$ and the lifetime τ of the donor (Table 1), the refraction index of toluene *n*, the donor-acceptor distance d_{DA} , and the orientation factor κ^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 Å for Cum1-C3, 7.3 Å for Cum3-C3, and 16.5 Å for Cum4-C3. The calculated k_{en}^{F} is 2×10¹² s⁻¹ for **Cum1-C3**, 5×10¹² s⁻¹ for **Cum3-C3**, and $1.5 \times 10^{11} \text{ s}^{-1}$ for **Cum4-C3**. The agreement with experimental values, $k_q > 2 \times 10^{11} \text{ s}^{-1}$ for **Cum1-C3** and **Cum3-C3** and $k_q =$ 1.3×10^{11} 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 Å) 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**C3**, 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 C3, 3.35 eV for Cum1, 3.22 eV for Cum3, 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 eV) and Cum4 (2.50 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 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 Cum2-¹C3 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⁻-C3⁺. In fact, C3 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 CH2Cl2 have the following half-wave potentials versus SCE: -1.30 V for Cum1; -1.06 V for Cum2; -1.24 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 Cum2 can be reduced at an energy 0.2-0.3 eV lower than all other coumarins, and as a consequence, the charge separated state level corresponding to Cum2⁻-C3⁺ 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 eV.^[35] The presence of a low lying charge separated state, Cum2⁻-C3⁺, 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, Cum2-¹C3, 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 C3 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 C3 and may be ascribed to the singlet excited state, ¹C3.^[9a] Differences in the spectra can be detected around 650-700 nm, where the C3 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 nm, 3 mJ), A = 0.65, of: C3 (---) and Cum2-C3 (--). 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 Cum2-¹C3, 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,^[9a] 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 α,β -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 Cum2--C3+, 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 corrole-coumarin dyads.

Experimental Section

grade solvents (MeCN, CH2Cl2, hexane, toluene) were distilled prior to

Synthesis

All chemicals were used as received unless otherwise noted. Reagent

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use. All reported NMR spectra were recorded on a 400 MHz or 500 MHz spectrometer unless otherwise noted. Chemical shifts (δ 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 SX-1 with THF as eluent. Mass spectra were obtained by EI or electrospray MS. The following compounds were prepared as described in the literature: **3**,^[36] **8**,^[24] **Cum1**,^[31] and **Cum4**.^[29]

6-Formyl-8-methoxy-3-methoxycarbonyl-2-oxo-2*H***-chromen** (4). To a stirred solution of aldehyde 2 (900 mg, 5 mmol) and dimethyl malonate (570 µL, 5 mmol) in hot MeOH (10 mL), pyrrolidine was added (5 drops) and the resulting mixture was refluxed for 5 h. Subsequently, the reaction mixture was cooled down to -17° C, the precipitate filtered off and washed with cold MeOH to afford 852 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 C₁₃H₁₀O₆:262 [*M*⁺]; found: 262.

10-(8-Methoxy-3-methoxycarbonyl-2-oxo-2H-chromen-6-yl)-5,15-bis(pentafluorophenyl)corrole (Cum1-C3). 5-(Pentafluorophenyl)dipyrromethane 3 (125 mg, 0.4 mmol) and coumarin 4 (crude, 52.4 mg, ~0.2 mmol) were dissolved in CH2Cl2 (3 mL). TFA (10 µL, 0.13 mmol) was added and the reaction mixture was stirred at RT for 1 h. Subsequently, Et₃N (18 µL, 0.13 mmol) was added and the resulting solution was diluted with CH₂Cl₂ to 312 mL. DDQ (118 mg, 0.52 mmol) dissolved in toluene (1 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 (CH₂Cl₂). Fractions containing the desired product were concentrated and rechromatographed (DCVC, SiO2, CH2Cl2). Crystallization from CHCl₃/hexanes gave 26 mg (15%) of the corrole Cum1-C3. $R_{\rm f} = 0.39$ (CH₂Cl₂/acetone = 98:2); UV/Vis (toluene): $\lambda = 307$, 417, 568, 615, 642 nm; ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): $\delta = (-3) - (-1)$ (br s, 3 H), 3.94 (s, 3 H, CO₂CH₃), 4.10 (s, 3 H, OCH₃), 7.98 (d, J=1.7 Hz, 1 H, Ar), 8.05 (d, J = 1.7 Hz, 1 H, Ar), 8.60–8.70 (m, 5 H, β -H+CH), 8.77 (d, J = 4.6 Hz, 2H, β -H), 9.17 ppm (d, J = 4.4 Hz, 2H, β -H); HRMS (ESI): m/z (%) calcd for C₄₃H₂₁F₁₀N₄O₅: 863.1347 [*M*+H⁺]; found: 863.1378; elemental analysis: calcd (%) for $C_{43}H_{21}F_{10}N_4O_5{:}\ C\,59.87,$ H 2.34, N 6.49; found: C 59.94, H 2.37, N 6.31.

6-Formyl-5-hydroxy-4-metoxycarbonyl-2-oxo-2H-chromen (6). 2,4-Dihydroxybenzaldehyde (5, 5.56 g, 40 mmol) and PPh₃ (10.6 g, 40 mmol) were dissolved in anhydrous toluene (100 mL). The reaction mixture was cooled down to -5°C and dimethyl acetylenedicarboxylate (4.94 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°C; IR (KBr): $\tilde{\nu} = 819$, 1019, 1268, 1650, 1743, 3085 cm⁻¹; ¹H NMR (400 MHz, $[D_6]$ DMSO, 25 °C, TMS): $\delta = 3.89$ (s, 3H, CO_2CH_3), 6.67 (s, 1H, CH), 7.12 (d, J=8.7 Hz, 1H, Ar), 8.02 (d, J=8.7 Hz, 1H, Ar), 10.03 (s, 1H, CHO), 12.30 ppm (brs, 1H, OH); ¹³C NMR (100 MHz, [D₆]DMSO, 25 °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 C₁₂H₈O₆: 248.0321 [*M*⁺]; found: 248.0331; elemental analysis: calcd (%) for C12H8O6: C 58.07, H 3.25; found: C 57.97, Н 3.25.

Methyl 6-(5,5-dimethyl-1,3-dioxan-2-yl)-5-hydroxy-2-oxo-2*H*-chromene-4-carboxylate (Cum2). A solution of coumarin 6 (300 mg, 1.2 mmol), 2,2dimethylpropane-1,3-diol and TsOH·H₂O (23 mg, 0.12 mmol) in toluene (50 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 mg, 58%). $R_{\rm f}$ =0.5 (hexane/ethyl acetate = 1:1); m.p.: 165 °C; UV/Vis (chloroform): λ ($\varepsilon \times 10^{-2}/\text{dm}^3\text{mol}^{-1}\text{ cm}^{-1}$) 301 (114); ¹H NMR (500 MHz, CDCl₃, 25 °C,

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TMS): δ =9.15 (s, 1H, OH), 7.40 (d, J=8.7 Hz, 1H, Ar), 6.88 (d, J= 8.7 Hz, 1H, Ar), 6.28 (s, 1H, CH=), 5.59 (s, 1H, CH), 3.95 (s, 3H, OCH₃), 3.83 (d, J=11.4 Hz, 2H, CH₂), 3.69 (d, J=11.2 Hz, 2H, CH₂), 1.27 (s, 3H, CH₃), 0.84 ppm (s, 3H, CH₃); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): δ =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 [C₁₇H₁₈O₇Na]: 357.0945; found: 357.0932; elemental analysis: calcd (%) for C₁₇H₁₈O₇: C 61.07, H 5.43; found C 61.11, H 5.56.

10-(5-Hydroxy-4-methoxycarbonyl-2-oxo-2H-chromen-6-yl)-5,15-bis(pentafluorophenyl)corrole (Cum2-C3). 5-(Pentafluorophenyl)dipyrromethane (3) (1.25 g, 4 mmol) and coumarin 6 (496 mg, 2 mmol) were dissolved in CH2Cl2 (30 mL). TFA (100 µL, 1.32 mmol) was added and the resulting mixture was stirred at RT for 1 h. Then Et₃N (181 µL, 0.04 mmol) was added, followed by CH_2Cl_2 (10 mL). DDQ (1.18 g, 5.2 mmol) was dissolved in a toluene/CH2Cl2 (1:1, 40 mL) mixture and both solutions were added simultaneously to CH2Cl2 (50 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 cm) silica pad (CH₂Cl₂). The fluorescent band was collected, evaporated, and rechromatographed (DCVC, SiO₂, CH₂Cl₂/hexane=3:2, then 4:1, CH₂Cl₂). Crystallization from CHCl₃/hexane gave 101 mg (6%) of the corrole **Cum2-C3**. $R_f = 0.43$ (CH₂Cl₂/acetone = 98:2); UV/Vis (toluene): $\lambda = 424$, 565, 611, 640 nm; ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): $\delta = (-3)$ -(-1) (brs, 3H), 3.75 (s, 3H, CO₂CH₃), 6.55 (s, 1H, CH), 7.30 (d, J= 8.5 Hz, 1H, Ar), 8.11 (d, J=8.5 Hz, 1H, Ar), 8.59 (d, 2H, J=4.2 Hz, β-H), 8.62 (d, J=4.7 Hz, 2H, β-H), 8.75 (d, J=4.7 Hz, 2H, β-H), 9.14 ppm (d, J = 4.2 Hz, 2H, β -H), signal from OH could not be identified; LRMS (EI): m/z (%) calcd for C₄₂H₁₈F₁₀N₄O₅: 848.1 [M⁺]; found: 848.0; elemental analysis: calcd (%) for $C_{42}H_{18}F_{10}N_4O_5{:}$ 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-2H-chromen (9). This compound was prepared exactly according to the procedure described for **6**. Starting from aldehyde **8** (1.52 g, 10 mmol), 1.53 g (59%) of the product was obtained. M.p.: 165–167 °C; IR (KBr): $\tilde{v}757$, 1148, 1580, 1617, 1658, 1722, 1751, 1806, 3080 cm⁻¹; ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 2.22 (s, 3 H, CH₃), 3.96 (s, 3 H, CO₂CH₃), 6.80 (s, 1 H, CH), 8.42 (s, 1 H, Ar), 10.13 (s, 1 H, CHO), 11.56 ppm (brs, 1 H, OH); ¹³C NMR (100 MHz, [D₆]DMSO, 25 °C, TMS): δ = 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 C₁₃H₁₀O₆: C 59.55, H 3.84; found: C 59.65, H 3.79.

$10 \hbox{-} (7 \hbox{-} Hydroxy \hbox{-} 4 \hbox{-} methoxy carbonyl \hbox{-} 8 \hbox{-} methyl \hbox{-} 2 \hbox{-} oxo \hbox{-} 2 H \hbox{-} chromen \hbox{-} 6 \hbox{-} yl) \hbox{-}$

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 g, 4 mmol) and coumarin **9** (524 mg, 2 mmol), 46 mg (3%) of the corrole **Cum3-C3** was obtained. R_f =0.54 (CH₂Cl₂/acetone =98:2); UV/Vis (toluene): λ =423, 564, 609, 634 nm; ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ =(-3)-(-1) (brs, 3H), 2.59 (s, 3H, CH₃), 3.78 (s, 3H, CO₂CH₃), 6.89 (s, 1H, CH), 8.55–8.70 (m, 5H, Ar+ β -H), 8.76 (m, 2H, β -H), 9.14 ppm (m, 2H, β -H), signal from OH couldn't be identified; HRMS (EI): *m/z* (%) calcd for C₄₃H₂₀F₁₀N₄O₅: 862.1274 [*M*⁺]; found: 862.1297.

Methyl 7-hydroxy-8-methyl-2-oxo-2*H*-chromene-4-carboxylate (Cum3). A solution of DMAD (615 μL, 5 mmol) in dry toluene (2 mL) was added dropwise for 15 min to a cooled (-5° C) solution of 2-methylresorcinol (7, 620 mg, 5 mmol) and triphenylphosphine (1.310 g, 5 mmol) in dry toluene (15 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 mg, 20%). R_t =0.3 (toluene/ethyl acetate=7:3); m.p.: 202°C; UV/Vis (THF): λ (ε×10^{-2/} dm³ mol⁻¹ cm⁻¹) 347 (107) nm; ¹H NMR (500 MHz, [D₆]DMSO, 25°C, TMS): δ =10.64 (s, 1H, OH), 7.73 (d, J=8.9 Hz, 1H, Ar), 6.89 (d, J=8.9 Hz, 1H, Ar), 6.56 (s, 1H, CH=), 3.92 (s, 3H, OCH₃), 2.17 ppm (s, 3H, CH₃); ¹³C NMR (125 MHz, [D₆]DMSO, 25°C, TMS): δ =164.5,

159.8, 159.5, 153.6, 143.5, 124.5, 112.7, 112.3, 111.2, 107.6, 53.0, 7.9 ppm; HR EI-MS: m/z (%) calcd. for $C_{12}H_{10}O_5$: 234.0528; found: 234.0520; elemental analysis: calcd (%) for $C_{12}H_{10}O_5$: 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 (3, 1.56 g, 5.0 mmol) and aldehyde 10 (505 mg, 2.5 mmol) in MeOH (250 mL), aqueous HCl (36 %, 12.5 mL) in H₂O (250 mL) was added and the resulting suspension was stirred at RT for 1 h. The reaction mixture was then extracted with CHCl₃ (2×50 mL), and the organic phases were washed with water (2×50 mL) and dried (Na₂SO₄). The drying agent was removed and the mixture was concentrated to 60 mL. DDQ (1.47 g, 6.5 mmol) was dissolved in toluene/CH2Cl2 (1:1, 60 mL) mixture and both solutions were added simultaneously to CH2Cl2 (50 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 cm) silica pad (CH₂Cl₂/hexane=1:1). The fluorescent band was collected, evaporated and rechromatographed (DCVC, SiO₂, CH₂Cl₂/hexane=1:4). Crystallization from hexane gave 475 mg (24%) of product. $R_{\rm f} = 0.62$ (CH₂Cl₂/ hexane=2:3); UV/Vis (toluene): λ ($\epsilon \times 10^{-3}$) 424 (106), 564 (16.8), 615 (9.8), 641 (6.67) nm; ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): $\delta = (-4)$ -(-1.5) (br s, 3H, NH), 0.37 (s, 9H, 3×CH₃), 7.87, 8.11 (AA'BB', J= 8.1 Hz, 2×2H, C₆H₄), 8.55 (br d, J=3.6 Hz, 2H, β-H), 8.66 (d, J=4.6 Hz, 2H, β-H), 8.71 (d, J=4.6 Hz, 2H, β-H), 9.08 ppm (d, J=4.2 Hz, 2H, β-H); LRMS (EI): m/z (%) calcd for $C_{42}H_{24}F_{10}N_4Si$: 802.2 [M^+]; found: 802; elemental analysis: calcd (%) for $C_{42}H_{24}F_{10}N_4Si;\ C\,62.84,\ H\,3.01,$ 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 mg, 75 µmol) in CHCl₃ (3 mL) TBAF (1 M solution in THF, 150 µL, 150 µmol) was added. The resulting mixture was stirred at RT for 2 h. The solvent was removed under reduced pressure and the residue was chromatographed (DCVC, SiO₂, CH₂Cl₂/hexane = 2:3, then 1:1). Crystallization from hexane gave 50 mg (91%) of the corrole **11**. $R_{\rm f}$ =0.52 (CH₂Cl₂/hexane=2:3); UV/Vis (toluene): λ =(ϵ ×10⁻³) 421 (103), 564 (15.9), 615 (9.4), 641 (6.29) nm; ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ =(-4)-(-1.5) (brs, 3H, NH), 3.30 (s, 1H, CH), 7.89, 8.14 (AA'BB', J=8.0 Hz, 2×2H, C₆H₄), 8.56 (br d, J=3.3 Hz, 2H, β -H), 8.67 (d, J=4.7 Hz, 2H, β -H); HRMS (EI): m/z (%) calcd for C₃₉H₁₆F₁₀N₄: 730.1215 [*M*⁺]; found: 730.1204.

6-Bromo-7-diethylamino-3-[(7-diethylamino-2-oxo-2H-chromen-3-yl)carbonyl]-4a,8a-dihydro-2H-chromen-2-on (14). To a stirred solution of aldehyde 12 (417 mg, 1.54 mmol) and ester 13 (488 mg, 1.54 mmol) in hot MeOH (60 mL), pyrrolidine (80 µL, 0.96 mmol) was added, followed by AcOH (60 $\mu L,\,0.96$ 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 °C; UV/Vis (toluene): $\lambda = 445$ nm; IR (KBr): 1133, 1190, 1198, 1351, 1508, 1589, 1617, 1721 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): $\delta = 1.13$ (t, J = 7.0 Hz, 6H, $2 \times CH_2CH_3$), 1.24 (t, J = 7.1 Hz, 6H, $2 \times CH_2CH_3$), 3.28 (q, J = 7.0 Hz, 4H, $2 \times CH_2CH_3$), 3.46 (q, J = 7.0 Hz, 4H, $2 \times CH_2CH_3$), 3.46 (q, J = 7.0 Hz, 4H, $2 \times CH_2CH_3$), 3.46 (q, J = 7.0 Hz, 4H, $2 \times CH_2CH_3$), 3.46 (q, J = 7.0 Hz, 4H, $2 \times CH_2CH_3$), 3.46 (q, J = 7.0 Hz, 4H, $2 \times CH_2CH_3$), 3.46 (q, J = 7.0 Hz, $4 \times CH_2CH_3$), $3.46 \times CH_3$), $3.46 \times CH_3$), $3.46 \times CH_3$), $3.46 \times CH_3$ 7.1 Hz, 4H, $2 \times CH_2CH_3$), 6.48 (d, J = 2.4 Hz, 1H, Ar), 6.62 (dd, ${}^{3}J =$ 9.0 Hz, ${}^{4}J$ = 2.4 Hz, 1 H, Ar), 6.94 (s, 1 H, Ar), 7.41 (d, J = 9.0 Hz, 1 H, Ar), 7.75 (s, 1H, Ar), 7.99 (s, 1H, CH), 8.29 ppm (s, 1H, CH); ¹³C NMR (125 MHz, CDCl₃, 25 °C, 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 C₂₇H₂₇N₂O₅Br: 538.1103 [M⁺⁺]; found: 538.1123.

Corrole Cum4-C3. Corrole **11** (144 mg, 198 μ mol), coumarin **14** (130 mg, 240 μ mol), Cs₂CO₃ (69 mg, 210 μ mol), Pd(OAc)₂ (11.0 mg, 50 μ mol) and PPh₃ (51 mg, 198 μ 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 °C for 24 h. The solvent was removed under reduced pressure and the residue was chromatographed (SiO₂, CH₂Cl₂, then CH₂Cl₂/acetone =98:2). Fractions containing the desired product were collected, evaporated and rechromatographed (SEC, THF). Crystallization from CHCl₃/hexane gave 70 mg (30%) of the cor-

role **Cum4-C3**. $R_{\rm f}$ =0.62 (CH₂Cl₂/acetone=95:5); UV/Vis (toluene): λ= 435, 566, 616, 640 nm; ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ= (-4)-(-1.5) (brs, 3H, NH), 1.25 (t, *J*=7.1 Hz, 6H, 2×CH₂CH₃), 1.40 (t, *J*=7.1 Hz, 6H, 2×CH₂CH₃), 3.46 (q, 7.1 Hz, 4H, 2×CH₂CH₃), 3.80 (q, *J*=7.1 Hz, 4H, 2×CH₂CH₃), 6.62 (d, *J*=2.0 Hz, 1H, Ar), 6.72 (s, 1H, Ar), 6.85 (dd, ³*J*=9.0 Hz, ⁴*J*=2.0 Hz, 1H, Ar), 7.69 (d, *J*=9.0 Hz, 1H, Ar), 7.79 (s, 1H, Ar), 8.00, 8.25 (AA'BB', *J*=7.9 Hz, 2×2H, C₆H₄), 8.35 (s, 1H, Ar), 8.47 (s, 1H, CH), 8.60 (brs, 2H, β-H), 8.76 (br s, 4H, β-H), 9.10 (br d, *J*=3.2 Hz, 2H, β-H). LRMS (FD): *m/z* (%) calcd for C₆₆H₄₂F₁₀N₆O₅: 1188.3 [*M*⁴]; found: 1188.3; elemental analysis: calcd (%) for C₆₆H₄₂F₁₀N₆O₅: 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 C3 with a $\Phi_{\rm fl}\!=\!0.14.^{[9a]}\,{
m Lu}$ 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 nm, 1.5 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 ps. $^{[\hat{37}]}$ 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 nm, 3.5 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 nm, 3 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^[32a] in toluene are: $r_{AD} = 7.2$ Å, $r_D = 5$ Å, $r_A = 3.5$ Å, $\epsilon_P = 17.9$ (the average of dichloromethane and benzonitrile dielectric constants) and $\epsilon_{S}\!=\!2.4,$ 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 CH₂Cl₂ (C. Erba RPE, distilled over P₂O₅ and stored under Ar pressure) with 0.1 \times (C₄H₉)₄NClO₄ (Fluka, puriss. crystallized from CH₃OH and vacuum dried). After Ar bubbling, cyclic voltammetries were performed at 0.1 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 cm²), 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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- a) D. Gust, T. A. Moore, A. L. Moore, Acc. Chem. Res. 2001, 34, 40-48; b) D. Holten, D. F. Bocian, J. S. Lindsey, Acc. Chem. Res. 2002, 35, 57-69; c) H. Imahori, J. Phys. Chem. B 2004, 108, 6130-6143; d) J. H. Alstrum-Avecedo, M. K. Brennaman, T. J. Meyer, Inorg. Chem. 2005, 44, 6802-6827; e) L. Flamigni, V. Heitz, J-P. Sauvage, Struct. Bonding 2006, 121, 217-261; f) S. Fukuzumi, Y. Kashiwagi, J. Porphyrins Phthalocyanines 2007, 11, 368-374; g) K-i. Yamanaka, M. Fujitsuka, Y. Araki, K. Tashiro, A. Sato, T. Yuzawa, T. Aida, J. Porphyrins Phthalocyanines 2007, 11, 397-405; h) M. R. Wasielewski, J. Org. Chem. 2006, 71, 5051-5066; i) L. Flamigni, J.-P. Collin, J. P. Sauvage, Acc. Chem. Res. 2008, 41, 857-871; j) A. S. D. Sandanayaka, N. K. Subbaiyan, R. Chitta, Y. Araki, O. Ito, F. D'Souza, J. Porphyrins Phthalocyanines 2008, 12, 857-865.
- [2] For reviews, see: a) S. G. Boxer, Biochim. Biophys. Acta Rev. Bioenerg. 1983, 726, 265–292; b) D. Gust, T. A. Moore, Science 1989, 244, 35–41; c) V. V. Borovkov, R. P. Evstigneeva, L. N. Strekova, E. I. Filippovich, Russ. Chem. Rev. 1989, 58, 602–619; d) D. Gust, T. A. Moore, Top. Curr. Chem. 1991, 159, 103–151; e) M. R. Wasielewski in Chlorophylls (Ed.: H. Scheer), CRC Press, Boca Raton, FL, 1991 pp. 269–286; f) M. R. Wasielewski, Chem. Rev. 1992, 92, 435–461; g) D. Gust, T. A. Moore, A. L. Moore, Acc. Chem. Res. 1993, 26, 198–205; h) H. Kurreck, M. Huber, Angew. Chem. 1995, 107, 929–947; Angew. Chem. Int. Ed. Engl. 1995, 34, 849–866; i) B. Sasabe, Y. Furusho, A. S. D. Sandanayaka, Y. Araki, N. Kihara, K. Mizuno, A. Ogawa, T. Takata, O. Ito, J. Porphyrins Phthalocyanines 2006, 10, 1346–1359; j) L. Flamigni, J. Photochem. Photobiol. C 2007, 8, 191–210.
- [3] a) R. Paolesse in *The Porphyrin Handbook, vol.* 2 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, 2000, pp. 201–232; b) S. Nardis, D. Monti, R. Paolesse, *Mini-Rev. Org. Chem.* 2005, 2, 355–372; c) D. T. Gryko, *Eur. J. Org. Chem.* 2002, 1735–1742; d) D. T. Gryko, J. P. Fox, D. P. Goldberg, *J. Porphyrins Phthalocyanines* 2004, 8, 1091–1105; e) C. Erben, S. Will, K. M. Kadish in *Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard). vol.2, Academic Press: San Diego, CA, 2000; pp. 233; f) R. Guilard, K. M. Kadish J-M. Barbe, C. Stern in *The Porphyrin Handbook II, Vol. 18* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard, New 14, Kedish, S. M. Smith, R. Guilard, J. Pol. 351; g) R. Paolesse, *Synlett* 2008, 2215–2230; h) I. Aviv, Z. Gross, *Chem. Commun.* 2007, 1987–1999; i) D. T. Gryko, *J. Porphyrins Phthalocyanines* 2008, *12*, 906–917; j) D. P. Goldberg, *Acc. Chem. Res.* 2007, *40*, 626–634.
- [4] a) B. Ramdhanie, C. L. Stern, D. P. Goldberg, J. Am. Chem. Soc. 2001, 123, 9447–9448; b) A. E. Meier-Callahan, A. J. Di Bilio, L. Simkhovich, A. Mahammed, I. Goldberg, H. B. Gray, Z. Gross, Inorg. Chem. 2001, 40, 6788–6793; c) Z. Gross, J. Biol. Inorg. Chem. 2001, 6, 733–738; d) N. Y. Edwards, R. A. Eikey, M. I. Loring, M. M. Abu-Omar, Inorg. Chem. 2005, 44, 3700–3708; e) C. A. Joseph, P. C. Ford, J. Am. Chem. Soc. 2005, 127, 6737–6743; f) J. P. Collman, H. J. H. Wang, R. A. Decréau, T. A. Eberspacher, C. J. Sunderland, Chem. Commun. 2005, 2497–2499; g) J.-M. Barbe, G. Canard, S. Brandès, R. Guilard, Angew. Chem. 2005, 117, 3163–3166; Angew. Chem. Int. Ed. 2005, 44, 3103–3106; h) M. Bröring, F. Brégier, E. C. Tejero, C. Hell, M. C. Holthausen, Angew. Chem. 2007, 119, 449–452; Angew. Chem. Int. Ed. 2007, 46, 445–448; i) A. J. McGown, W. D. Kerber, H. Fujii, D. P. Goldberg, J. Am. Chem. Soc. 2009, 131, 8040–8048.
- [5] a) Z. Gross, N. Galili, I. Saltsman, Angew. Chem. 1999, 111, 1530–1533; Angew. Chem. Int. Ed. 1999, 38, 1427–1429; b) R. Paolesse, S. Nardis, F. Sagone, R. M. Khoury, J. Org. Chem. 2001, 66, 550–556; c) R. P. Briñas, C. Brückner, Synlett 2001, 442–444; d) D. T. Gryko, K. Jadach, J. Org. Chem. 2001, 66, 4267–4275; e) J. M. Barbe, F. Burdet, E. Espinoza, C. P. Gros, R. Guilard, J. Porphyrins Phthalocyanines 2003, 7, 365–374; f) D. T. Gryko, M. Tasior, B. Koszarna, J.

Porphyrins Phthalocyanines **2003**, *7*, 239–248; g) G. R. Geier, III., J. F. B. Chick, J. B. Callinan, C. G. Reid, W. P. Auguscinski, *J. Org. Chem.* **2004**, *69*, 4159–4169; h) C. Jeandon, R. Ruppert, H. J. Callot, *Chem. Commun.* **2004**, 1090–1091; i) M. Bröring, S. Köhler, *J. Porphyrins Phthalocyanines* **2008**, *12*, 1111.

- [6] a) I. Saltsman, A. Mahammed, I. Goldberg, E. Tkachenko, M. Botoshansky, Z. Gross, J. Am. Chem. Soc. 2002, 124, 7411-7420; b) R. Paolesse, S. Nardis, M. Venanzi, M. Mastroianni, M. Russo, F. R. Fronczek, M. G. H. Vicente, Chem. Eur. J. 2003, 9, 1192-1197; c) S. Hiroto, K. Furukawa, H. Shinokubo, A. Osuka, J. Am. Chem. Soc. 2006, 128, 12380-12381; d) J. F. B. Barata, A. M. G. Silva, M. G. P. M. S. Neves, A. C. Tomé, A. M. S. Silva, J. A. S. Cavaleiro, Tetrahedron Lett. 2006, 47, 8171-8174; e) F. Mandoj, M. Stefanelli, S. Nardis, M. Mastroianni, F. R. Fronczek, K. M. Smith, R. Paolesse, Chem. Commun. 2009, 1580-1582.
- [7] J. Shao, J. Shen, Z. Ou, W. E, B. Koszarna, D. T. Gryko, K. M. Kadish, *Inorg. Chem.* 2006, 45, 2251–2265.
- [8] a) C. Di Natale, D. Salimbeni, R. Paolesse, A. Macagnano, A. Damico, Sens. Actuators B 2000, 65, 220; b) J-M. Barbe, G. Canard, S. Brandès, F. Jérôme, G. Dubois, R. Guilard, Dalton Trans. 2004, 1208–1214; c) J. Radecki, I. Stenka, E. Dolusic, W. Dehaen, J. Plavec, Comb. Chem. High Throughput Screening 2004, 7, 375–381; d) Y. S. Balazs, I. Saltsman, A. Mahammed, E. Tkachenko, G. Golubkov, J. Levine, Z. Gross, Magn. Res. Chem. 2004, 42, 624–635; e) K. M. Kadish, J. Shao, Z. Ou, L. Frémond, R. Zhan, F. Burdet, J-M. Barbe, C. P. Gros, R. Guilard, Inorg. Chem. 2005, 127, 2883–2887; g) Z. Ou, J. Shen, J. E. W. Shao, M. Gałęzowski, D. T. Gryko, K. M. Kadish, Inorg. Chem. 2007, 46, 2775–2786; h) C. Capar, K. E. Thomas, A. Ghosh, J. Porphyrins Phthalocyanines 2008, 12, 964.
- [9] a) B. Ventura, A. Degli Esposti, B. Koszarna, D. T. Gryko, L. Flamigni, *New J. Chem.* **2005**, *29*, 1559–1566; b) T. Ding, E. A. Alemán, D. A. Mordarelli, C. J. Ziegler, *J. Phys. Chem. A* **2005**, *109*, 7411–7417; c) D. Kowalska, X. Liu, U. Tripathy, A. Mahammed, Z. Gross, S. Hirayama, R. P. Steer, *Inorg. Chem.* **2009**, *48*, 2670–2676.
- [10] a) L. Flamigni, B. Ventura, M. Tasior, D. T. Gryko, *Inorg. Chim.* Acta 2007, 360, 803-813; b) M. Tasior, D. T. Gryko, M. Cembor, J. S. Jaworski, B. Ventura, L. Flamigni, New J. Chem. 2007, 31, 247-259; c) L. Flamigni, B. Ventura, M. Tasior, T. Becherer, H. Langhals, D. T. Gryko, Chem. Eur. J. 2008, 14, 169-183; d) C. P. Gros, F. Brisach, A. Meristoudi, E. Espinoza, R. Guilard, P. D. Harvey, Inorg. Chem. 2007, 46, 125-135; e) M. Tasior, D. T. Gryko, J. Shen, K. M. Kadish, T. Becherer, H. Langhals, B. Ventura, L. Flamigni, J. Phys. Chem. C 2008, 112, 19699-19709; f) F. D'Souza, R. Chitta, K. Ohkubo, M. Tasior, N. K. Subbaiyan, M. E. Zandler, M. K. Rogacki, D. T. Gryko, S. Fukuzumi, J. Am. Chem. Soc. 2008, 130, 14263-14272.
- [11] a) The Chemistry of Heterocyclic Compounds, Vol. 31-Chromenes, Chromanones, and Chromones, (Ed.: Gwynn P. Ellis), Wiley, Hoboken, NJ; b) K. H. Drexhage in Dye Lasers (Ed.: F. P.Schafer), Springer, New York, 1977.
- [12] L. Chen, T.-S. Hu, Z.-J. Yao, Eur. J. Org. Chem. 2008, 6175-6182.
- [13] a) A. R. S. Koefod, K. R. Mann, *Inorg. Chem.* **1989**, *28*, 2285–2290;
 b) B. S. Tasch, C. Brandstatter, F. Meghdadi, G. Leising, G. Froyer, L. Athouel, *Adv. Mater.* **1997**, *9*, 33–36.
- [14] C. A. E. Siegrist, H. Hefti, H. R. Mayer, E. Schmidt, *Rev. Prog. Color.* 1987, 17, 39–55.
- [15] a) D. J. Yee, V. Balsanek, D. Sames, J. Am. Chem. Soc. 2004, 126, 2282–2283; b) K. Sivakumar, F. Xie, B. M. Cash, S. Lung, H. N. Barnhill, Q. Wang, Org. Lett. 2004, 6, 4603–4606.
- [16] A. Elangovan, J-H. Lin, S-W. Yang, H.-Y. Hsu, T.-I. Ho, J. Org. Chem. 2004, 69, 8086–8092.

- [17] M.-S. Schiedel, C. A. Briehn, P. Bäuerle, Angew. Chem. 2001, 113, 4813–4816; Angew. Chem. Int. Ed. 2001, 40, 4677–4680.
- [18] a) S. L. Gilat, A. Andronov, J. M. J. Fréchet, Angew. Chem. 1999, 111, 1519–1524; Angew. Chem. Int. Ed. 1999, 38, 1422–1427;
 b) J. M. Serin, D. W. Brousmiche, J. M. J. Fréchet, J. Am. Chem. Soc. 2002, 124, 11848–11849; c) T. Akasaka, T. Mutai, J. Otsuki, K. Araki, Dalton Trans. 2003, 1537–1544; d) J: H. Hurenkamp, W. R. Browne, R. Augulis, A. Pugžlys, P. H. M. van Loosdrecht, J. H. van Esch, B. L. Feringa, Org. Biomol. Chem. 2007, 5, 3354–3362;
 e) M. J. Brites, C. Santos, S. Nascimento, B. Gigante, H. Luftmann, A. Fedorov, M. N. Berberan-Santos, New J. Chem. 2006, 30, 1036–1045.
- [19] a) W. Lin, L. Long, J. Feng, B. Wang, C. Guo, *Eur. J. Org. Chem.* 2007, 4301; b) P. K. Hania, D. J. Heijs, T. Bowden, A. A. Pugžlys, J. H. van Esch, J. Knoester, K. Duppen, *J. Phys. Chem. B* 2004, *108*, 71–81.
- [20] a) J. Duff, E. Bills, J. Chem. Soc. 1941, 547; b) W. E. Smith, J. Org. Chem. 1972, 37, 3972; c) L. F. Lindoy, G. V. Meehan, N. Svenstrup, Synthesis 1998, 1029.
- [21] D. T. Gryko, B. Koszarna, Synthesis 2004, 2205.
- [22] D. T. Gryko, M. Tasior, T. Peterle, M. Bröring, J. Porphyrins Phthalocyanines 2006, 10, 1360.
- [23] a) I. Yavari, M. Adib, L. Hojabri, *Tetrahedron* 2001, *57*, 7537–7540;
 b) I. Yavari, M. Adib, L. Hojabri, *Tetrahedron* 2002, *58*, 6895–6899;
 c) I. Yavari, R. Amiri, M. Haghdadi, *Phosphorus Sulfur Elem.* 2004, *179*, 2163–2168;
 d) A. Ramazani, A. R. Kazemizadeh, E. Ahmadi, N. Noshiranzadeh, A. Souldozi, *Curr. Org. Chem.* 2008, *12*, 59–82.
- [24] a) N. Takeuchi, T. Kasama, Y. Aida, J. Oki, I. Maruyama, *Chem. Pharm. Bull.* **1991**, *36*, 1415–1421; b) L. Shah, *J. Chem. Soc.* **1938**, 1828–1831.
- [25] S. F. Nielsen, S. B. Christensen, G. Cruciani, A. Kharazmi, T. Liljefors, J. Med. Chem. 1998, 41, 4819.
- [26] P. D. Rao, S. Dhanalekshmi, B. J. Littler, J. S. Lindsey, J. Org. Chem. 2000, 65, 7323.
- [27] B. Koszarna, D. T. Gryko, J. Org. Chem. 2006, 71, 3707.
- [28] J. E. T. Corrie, V. R. N. Munasinghe, W. Rettig, J. Heterocyclic Chem. 2000, 37, 1447.
- [29] D. P. Specht, P. A. Martic, S. Farid, Tetrahedron 1982, 38, 1203.
- [30] E. Shirakawa, T. Kitabata, H. Otsuka, T. Tsuchimoto, *Tetrahedron* 2005, 61, 9878.
- [31] C. N. O'Callaghan, T. B. H. McMurry, C. J. Cordin, J. Chem. Res. Miniprint 1990, 5, 901–922.
- [32] L. Flamigni, D. T. Gryko, Chem. Soc. Rev. 2009, 38, 1635-1646.
- [33] Th. Förster, Discuss. Faraday Soc. 1959, 27, 7-17.
- [34] D. L. Dexter, J. Chem. Phys. 1953, 21, 836-850.
- [35] a) A. Weller, Z. Phys. Chem. Wiesbaden, **1982**, 133, 93–98; b) N. Mataga, H. Chosrowjan, S. Taniguchi, Y. Shibata, N. Yoshida, A. Osuka, T. Kikuzawa, T. Okada, J. Phys. Chem. A **2002**, 106, 12191–12201.
- [36] J. K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise, J. S. Lindsey, Org. Process Res. Dev. 2003, 7, 799.
- [37] L. Flamigni, B. Ventura, A. I. Oliva, P. Ballester, *Chem. Eur. J.* 2008, 14, 4214–4224 and references therein.
- [38] L. Flamigni, A. M. Talarico, S. Serroni, F. Puntoriero, M. J. Gunter, M. R. Johnston, T. P. Jeynes, *Chem. Eur. J.* 2006, *12*, 2649–2659 and references therein.
- [39] L. Flamigni, J. Phys Chem. 1992, 96, 3331-3337.
- [40] CS Chem. 3D Ultra CambridgeSoft. Com, Cambridge MA, USA, 2000.
- [41] Matlab 5.2. The MathWorks Inc. Natik Ma 01760, USA, 1998.

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