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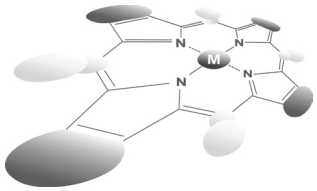

Corroles bearing diverse coumarin units — synthesis and optical properties

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Dedicated to Professor Karl M. Kadish on the occasion of his 65th birthday

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ABSTRACT: Two strategies were shown to be efficient in the construction of corroles with appended coumarin units. Direct condensation of formyl-coumarins with dipyrromethanes leads to a diverse range of *trans*-A_2B-corroles in moderate yields. We showed that the strategy consisting of synthesis of various hydroxycoumarins followed by nucleophilic aromatic substitution with pentafluorobenzaldehyde and subsequent condensation of the resulting coumarin-aldehyde with dipyrromethanes is the most general methodology for the preparation of such dyads. The second, more demanding but also more efficient approach is based on Sonogashira coupling of ethynylphenylcorroles with suitably functionalized bromocoumarins. A broad range of structurally diverse coumarins were employed with absorption ranging from 300 to 460 nm. Spectroscopic properties of all eight dyads studied suggest that the linker components are weakly electronically coupled.

KEYWORDS: corroles, coumarin, synthesis, fluorescence, dipyrromethanes.

INTRODUCTION

Corroles, one carbon shorter analogs of porphyrins, emerged a few years ago as an independent area of research [1]. First reported in 1965 [2], they possess the skeleton of corrin (macrocycle found in vitamin B_{12}) with three *meso*-carbons between the four pyrrole rings. Recent synthetic breakthroughs have made these macrocycles readily available [3]. When compared with porphyrins, these tribasic aromatic macrocycles exhibit interesting properties including lower oxidation potentials [4], higher fluorescence quantum yields, larger Stokes shift, and more intense absorption of red light [5]. Although less stable compared to analogous porphyrins, assemblies of appropriately functionalised corroles with other redox- and photo-active moieties for different applications have recently begun to emerge [6]. Their coordination chemistry, ring-functionalization and biomedical applications have been the most active areas of research in recent years [7–9]. In spite of these new applications, corroles continue to be a synthetic challenge. Although in many cases both the synthesis of *meso*-substituted corroles, as well as their derivatisation have been developed to a useful level, more complex cases are still problematic. In particular, in [2+1] condensation between dipyrromethanes and aldehydes, more complex structures have proven to be difficult to assemble due to the specific reactivity and/or poor solubility of these building blocks [10]. Still, this methodology is undoubtedly the most general one to prepare a variety of complex corroles [6]. As a part of a broader program in the chemistry of corrole-containing assemblies, we aimed to synthesize a library of covalently linked corrole-coumarin dyads. Coumarins as the counterpart were chosen due to their excellent and well-documented photochemical and photophysical behavior [11]. Coumarin dyes, owing to their intense fluorescence,

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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], but only few reports have been published on the photophysical properties of coumarin-porphyrinoid conjugates [18].

The idea of combining corroles and coumarins in one molecule is very attractive, and our previous report on this topic demonstrated that efficient energy transfer occurred between coumarin and corroles in such dyads [19]. Further progress in this area has been hindered due to increasing difficulties associated with the synthesis of such compounds. In this manuscript, we present recent advances and new strategies for the synthesis of coumarin-corroles with variable structure.

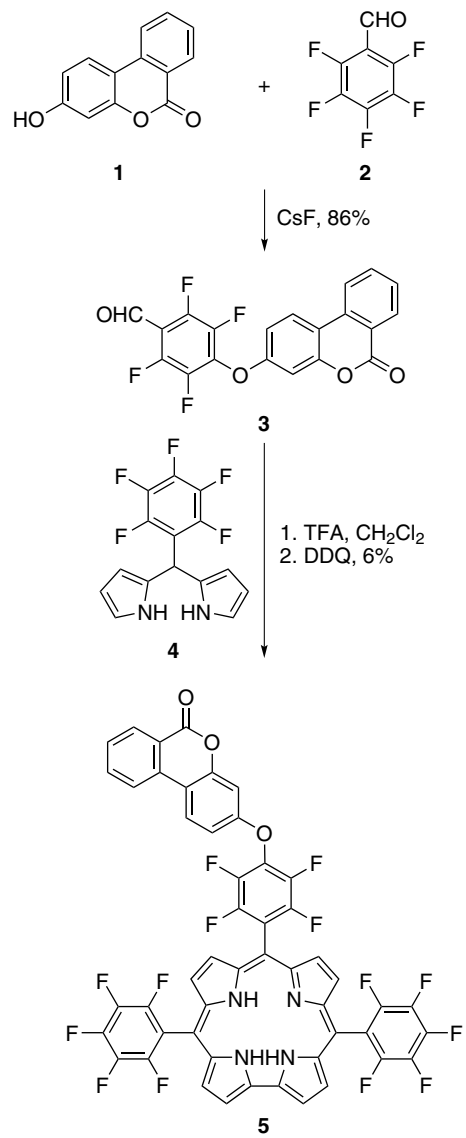
RESULTS AND DISCUSSION

Design and synthesis

Trans-A_2B-corroles bearing a coumarin moiety attached to the *meso*-10-position of corrole were chosen for our studies. This suitable structure benefits from efficient, general synthetic procedures developed in the last 10 years. We focused our investigation mainly on π-expanded coumarins which are able to absorb green light. Two pentafluorophenyl units were intended to be introduced at positions 5 and 15 since they secure good photostability of the corrole core for photophysical characterization [6]. The pentafluorophenyl group appeared to be the best choice due to the strong electron-withdrawing effect, imparting high solubility, lack of interference with spectroscopic properties and susceptibility to further transformations. Among many ways to achieve π-expansion of coumarin's chromophore, we focused on selected types which in our opinion provide compounds possessing interesting photophysical properties. Several issues merit particular consideration when contemplating the synthesis of complex corroles. From the standpoint of synthetic efficiency, in analogy to porphyrins, two general strategies are possible. The first starts with the synthesis of the corrole followed by modifications of the peripheral substituents. The second strategy starts with the preparation of an elaborated aldehyde which can then be used in the corrole-forming reaction. Given the moderate stability of corroles, it is desirable to gain significant relief from corrole manipulations. During the attempts to synthesize these bichromophoric systems, we followed both approaches.

One of the strategies which we planned to investigate was the synthesis of modified coumarin possessing a phenol unit followed by nucleophilic aromatic substitution of one fluorine atom in pentafluorobenzaldehyde. The potential advantages of this approach would be as follows: (a) von Pechmann-type condensation typically gives rise directly to hydroxycoumarins (without the need for laborious functionalization) and (b) corroles bearing tetrafluoroalkoxysubstituent at the *meso*-position should have higher oxidation potential, hence greater stability against light and oxygen.

Attempts to synthesize coumarin-derived aldehydes and transform them into corroles were initiated by the preparation of benzo[*c*]coumarin **1** synthesized using the Hurtley methodology [21], which was subsequently transformed into an aldehyde using conditions developed by us for selective nucleophilic substitution of pentafluorobenzaldehyde (**2**) by phenols [26]. The reaction went smoothly under standard conditions affording aldehyde **3** in 86% yield (Scheme 1). Reaction of this aldehyde with 5-(pentafluorophenyl)dipyrromethane (**4**) under conditions previously optimized for electron-deficient dipyrromethanes [27] afforded corrole **5** (Scheme 1). The yield was disappointingly low (6%) in spite of the fact that coumarin **3** does not possess a reactive, polarized carbon–carbon double bond which could act as a Michael



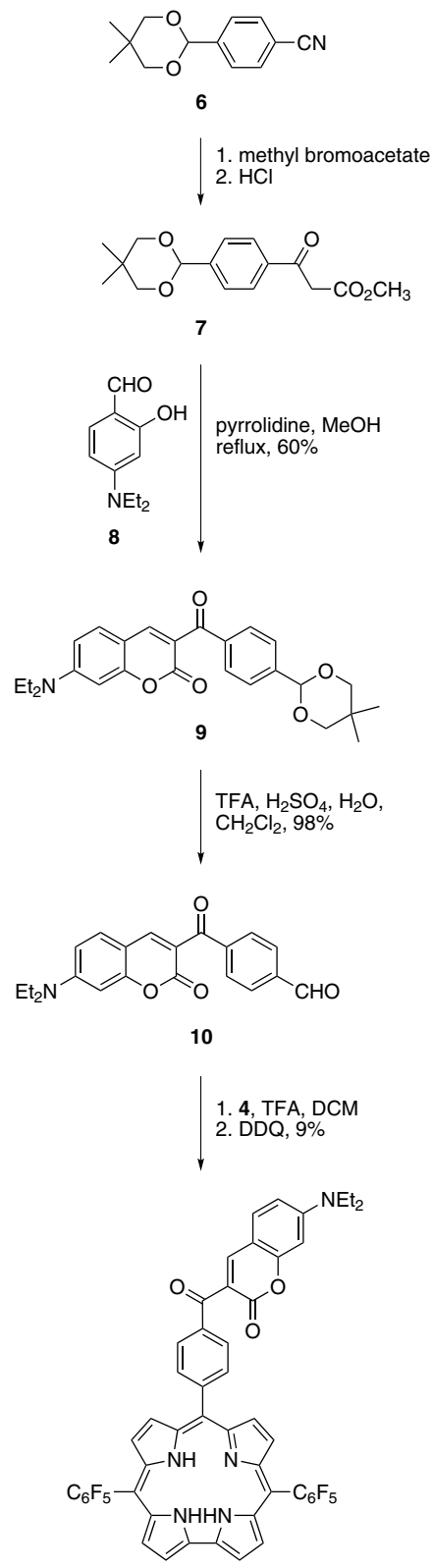
Scheme 1.

acceptor in possible side-reactions with the electron-rich pyrrole moiety.

The main effort of our investigation was focused on push-pull type structures with strong electron-donating groups at position 7 and a strong electron-withdrawing group at position 3. This type of coumarin architecture usually results in a bathochromic shift of absorption, a significant Stokes shift, strong fluorescence, and also the presence of a highly reactive α,β-unsaturated system (which can interfere with the Friedel-Crafts reaction of aldehydes with pyrrole derivatives). Coumarin structures have been modified/expanded to achieve absorption of blue-green light, which is advantageous in terms of further utilization models for energy transfer studies.

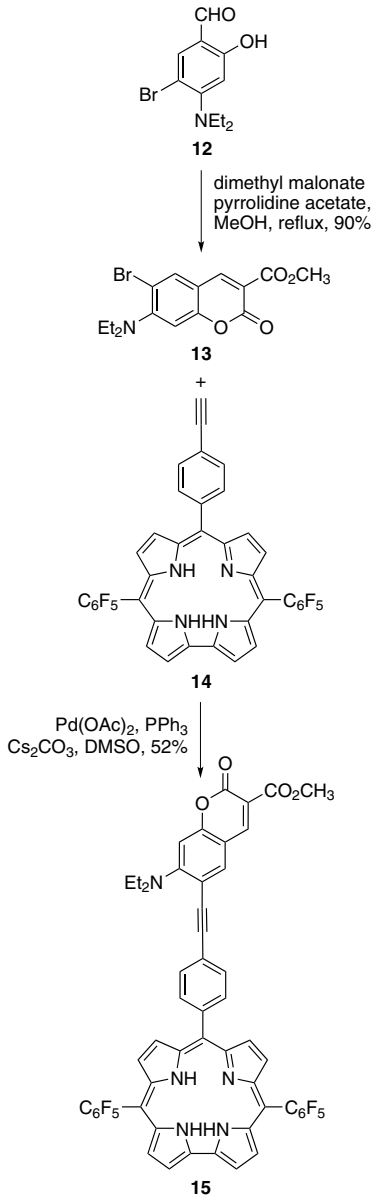
Along these lines, our next goal was to synthesize push-pull formyl-coumarin **10** (Scheme 2). The synthesis of compound **10** started with the Blaise reaction [28] as a key step (Scheme 2). The resulting β-ketoester **7** was subjected to the Knoevenagel reaction with aldehyde **8** which led to closing the ring and the formation of ketocoumarin **9**. The removal of the protecting group, followed by condensation with dipyrromethane **4**, afforded corrole **11** in 9% yield (Scheme 2). The presence of a second reactive carbonyl group in the structure of aldehyde **10** probably contributed to this result. This low yield achieved when the corrole-forming step was performed *via* condensation of coumarin-derived aldehydes prompted us to seek alternative ideas for the preparation of even more complex coumarin-corroles. In order to avoid this problem, we decided to synthesize coumarins suitable for Sonogashira coupling. We expected this strategy to be more flexible and efficient. We designed two bromocoumarins **13** and **17** as suitable models. Coumarin **13** was prepared from aldehyde **12** [23] *via* a classical approach (Scheme 3). The synthesis of derivative **17** required the condensation of β-ketoester **16** [24] with 5-bromosalicylaldehyde (Scheme 4). Easily available corrole **14** [19] was coupled with both bromo-coumarins **13** and **17** under copper-free conditions [29] in order to prevent metallation of the macrocycle ring. The expected bichromophoric systems were prepared in yields of 52% and 55%, respectively (Schemes 3 and 4).

Another paradigm for π-expansion of coumarins was based on conjugating another aromatic unit *via* the carbon–carbon double bond at position 4. One of the advantages of this strategy is good availability of the required building blocks (*i.e.*, coumarins bearing a methyl group at position 4) *via* the von Pechmann reaction. This, in turn, combined with access to an almost unlimited number of aromatic aldehydes, allowed for modular design of the final compounds. Based on a slightly modified procedure developed by Tkach *et al.* [25] for condensation of aldehydes with 4-methylcoumarins, we prepared aldehyde **22** which was subsequently condensed with pentafluorophenyldipyrromethane affording corrole **24** in 17% yield (Scheme 5). The isolated dyad was stable

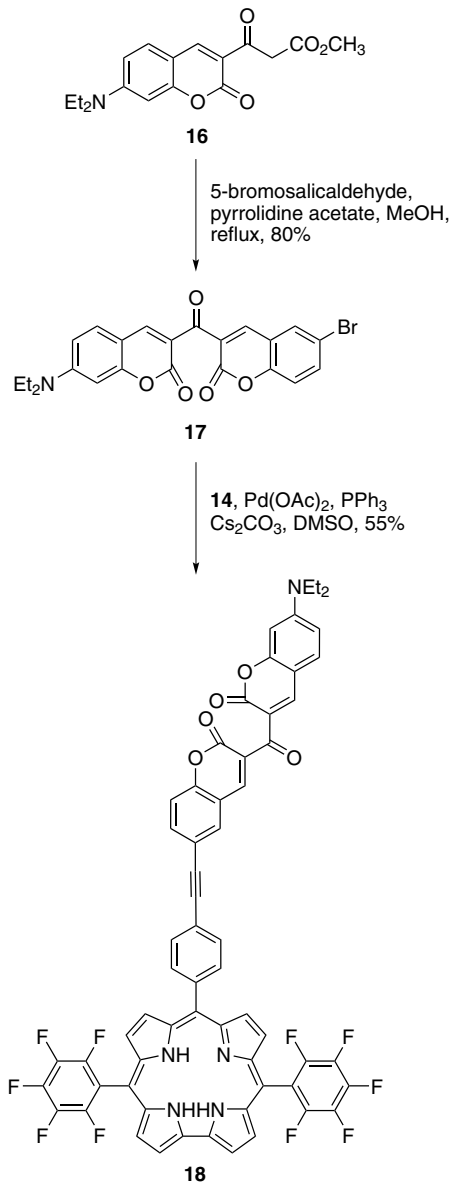


Scheme 2.

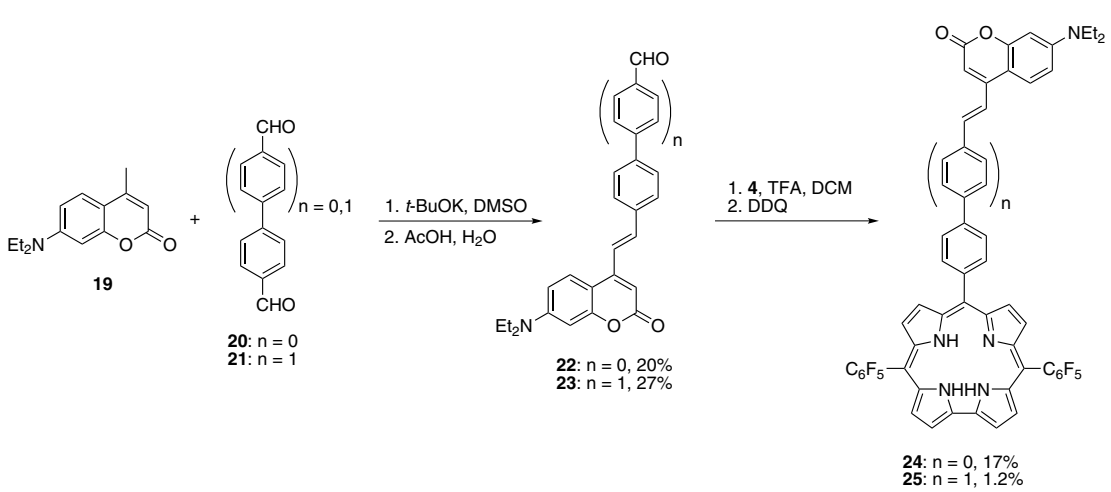
and easy to purify. Encouraged by this result, we decided to change the distance between the corrole and coumarin by introducing an additional phenylene linker. While the synthesis of analog **23** was quite straightforward, its



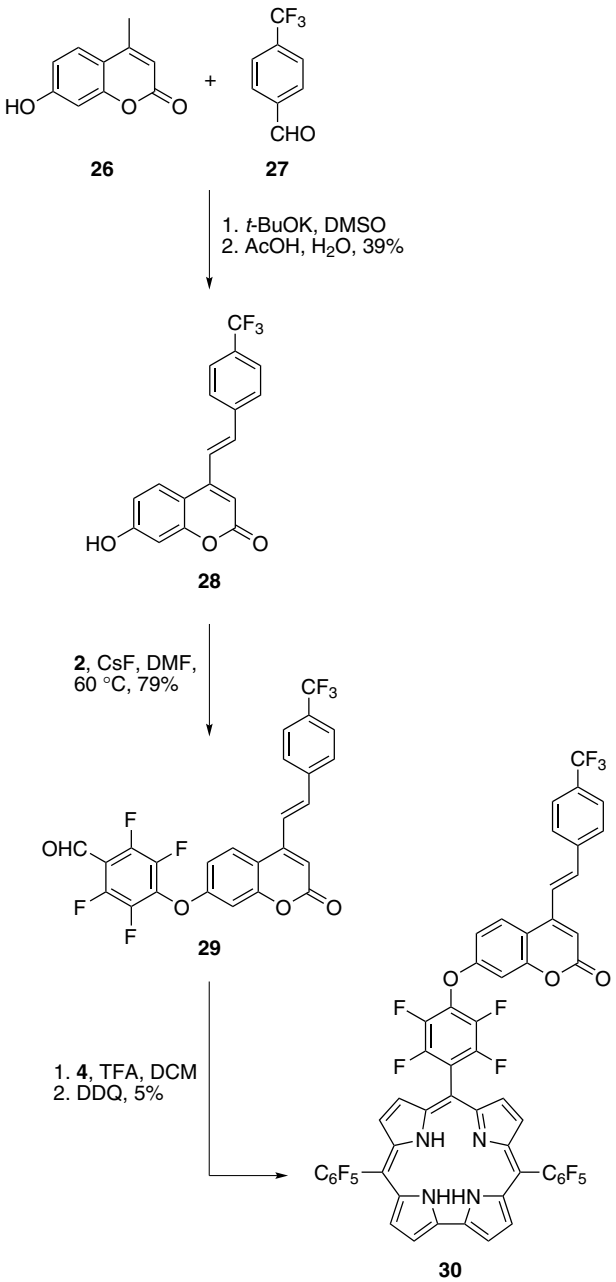
Scheme 3.



Scheme 4.



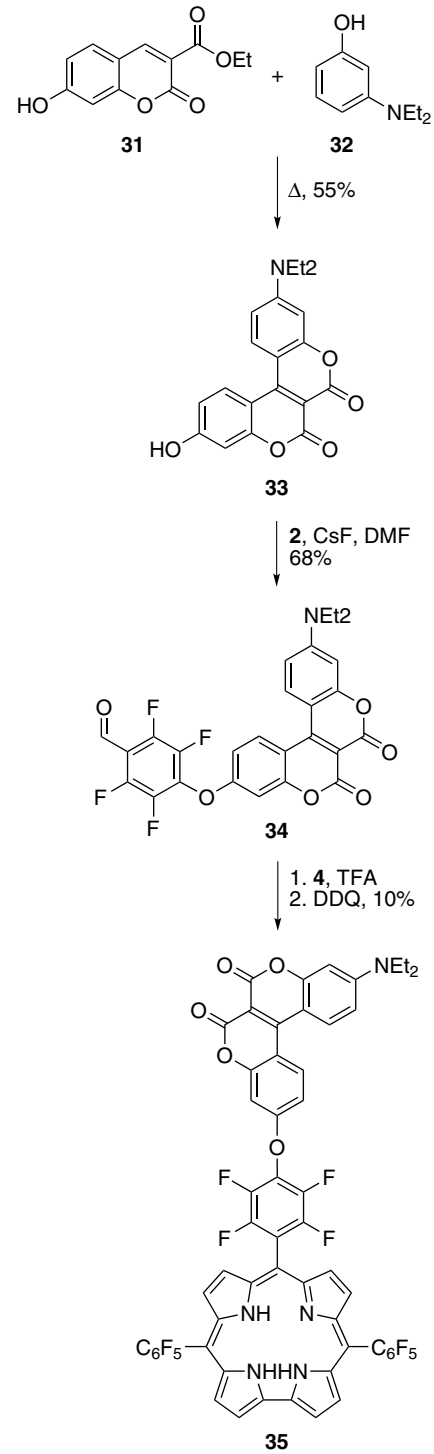
Scheme 5.



Scheme 6.

condensation with dipyrromethane **4** gave the required corrole **25** in a yield of only 1.2%.

This inclined us to think about an alternative way to link such π-expanded coumarins to the corrole core. We reasoned that if coumarins possess a free OH group, the nucleophilic substitution with C_6F_5CHO [26] can lead to better results. It has been noted by Tkach that only electron-poor aldehydes react with 4-methylcoumarins to give styril coumarins in good yields. Indeed, the condensation of coumarin **19** with *p*-hydroxybenzaldehyde did not lead to the expected product. Since the reaction of coumarin **19** and pentafluorobenzaldehyde under *t*-BuOK/DMSO conditions gave a mixture of tarry products, we turned our attention to styrilcoumarins derived from 4-methylumbelliferone (**26**). Typically, such compounds are synthesized by the reaction of the appropriate aldehyde with coumarinyl-4-acetic acids. We decided to study if Tkach's procedure could be applied to 4-methylumbelliferone (**26**) as well. To our delight, the reaction with 4-trifluoromethylbenzaldehyde (**27**) gave the expected product **28** in moderate yield (Scheme 6). The resulting phenol **28** was transformed into an aldehyde by the reaction with pentafluorobenzaldehyde (**2**) in the presence of cesium fluoride at a slightly elevated



Scheme 7.

temperature. Subsequent condensation with dipyrromethane **4**, followed by oxidation with DDQ gave, in 13% yield, corrole-coumarin dyad **30** of a completely different architecture compared to compounds **24** and **25**.

Recently, Högberg *et al.* [30], and Kovtun and coworkers [31] discovered two routes to a unique type of π-expanded coumarins (Scheme 7). These compounds are comprised of two coumarin units annelated with C3–C4 bonds. The resulting dyes strongly absorb blue-green light and have intense fluorescence. Using the general approach developed by Kovtun *et al.*, we synthesized new biscoumarin **33**, possessing a hydroxyl group, which underwent a reaction with pentafluobenzaldehyde resulting in the formation of aldehyde **34**. This aldehyde reacted with dipyrromethane **4** under typical conditions to give corrole **35** in 10% yield (Scheme 7).

The survey of various strategies leading to dyads comprised of coumarin and corrole units clearly proves that even complex formyl-coumarins react with dipyrromethanes in [2+1] condensation; however, the yield of macrocyclic products rarely exceeds 10%. On the other hand, Sonogashira coupling of ethynylcorroles with halogenocoumarins is a more efficient approach and can give consistently higher yields of the desired products.

The spectroscopic properties of the prepared compounds are collected in Table 1. The absorption of π-expanded coumarins is very strong, especially for compounds **9**, **23** and **33** (ε > 30000, Fig. 1). The absorption of coumarins **22** and **23**, although very intense, was not so bathochromically shifted as that of coumarins **17**, **29** and **33** (Table 1). The influence of the presence of coumarin units on the absorption spectra of dyads depended on the type of linkage, as well as on the absorption maximum of the coumarin counterpart. For corroles **5**, **30** and **35,** where both units are not directly linked but are separated by a moderately flexible linker, the influence was not so pronounced. Still, there was a characteristic hipsochromic shift in the Soret band in the absorption spectra all these corroles (λ_{max} = 408 nm), which originated from the overlap of the spectra of the corrole and coumarin units (Fig. 1, Table 1). The analysis of the spectra of corroles **11**, **15**, **18**, **24** and **25**, where modified coumarins were directly attached to the *meso*-10-position of the corrole core, confirmed the previous observation that due to substantial steric hindrance, there is no direct electronic communication between both units. The comparison of the absorption maxima with the spectra of corrole **14** or 5,15-bis(pentafluorophenyl)-10-(4-methylphenyl)corrole [5a] showed that the only difference resulted from the partial overlap of the Soret band with the absorption of coumarins in the violet-blue region (Table 1, Fig. 1). In the absorption of dyad **18,** one can easily see the broadening of the Soret band

Table 1. Spectroscopic data for coumarins and coumarin-corroles

Compound	Solvent	λ_{abs}, nm	$\varepsilon \times 10^{-3}$ [a]	λ_{em}, nm
3	CH_2Cl_2	301	18.0	380
5	CH_2Cl_2	301, 408, 562, 604	145.4	645
9	CH_2Cl_2	426	35.0	480
11	CH_2Cl_2	298, 421, 563, 612	13.1	656
13	CH_2Cl_2	397	2.2	518
14[b]	Toluene	421, 564, 615, 641	103	658
15	CH_2Cl_2	292, 422, 563, 614	140	655
17	CH_2Cl_2	430	58	nd[e]
18	CH_2Cl_2	426, 563, 612	143.6	655
19[c]	CH_2Cl_2	363	9.9	433
22[d]	THF	400	8	494
23	CH_2Cl_2	341	41.9	430, 550
24	CH_2Cl_2	305, 413, 563, 612	417	658
25	CH_2Cl_2	413, 652, 613	35	573
26	THF	475	32	574
28	CH_3CN	308	22	491
29	DMSO	432	2.5	457
30	CH_2Cl_2	308, 408, 562, 604	123	645
33	CH_3CN	367, 444	32.7	508
34	CH_3CN	342, 455	32.1	527
35	CH_2Cl_2	408, 459, 562, 604	983.1	646

[a] For corroles ε refers to intensity of Soret band. [b] Data from Ref. 19. [c] Data from Ref. 32. [d] Data from Ref. 25. [e] Not detectable.

(which for typical *meso*-substituted corroles ends up at ~460 nm) which originated from the strong absorption of the keto-bis-coumarin unit (Fig. 2).

The novel annelated biscoumarin **33** displayed intriguing spectroscopic properties, since the addition of the auxochrome group (OH) resulted in a hipsochromic rather than a bathochromic shift of absorption (λ_{max} of the analogous biscoumarin lacking a hydroxyl group was around 455 nm) [31]. In a way, these compounds behaved like a push-pull system. Replacing the strongly electron-donating hydroxyl group with a $OHCC_6F_4O$ group (**33** → **34**) resulted in a 11 nm bathochromic shift of absorption and emission which further confirmed this conclusion (Table 1). Strong absorption of coumarin **34** in the blue region was also clearly visible on the spectrum of dyad **35** (Table 1).

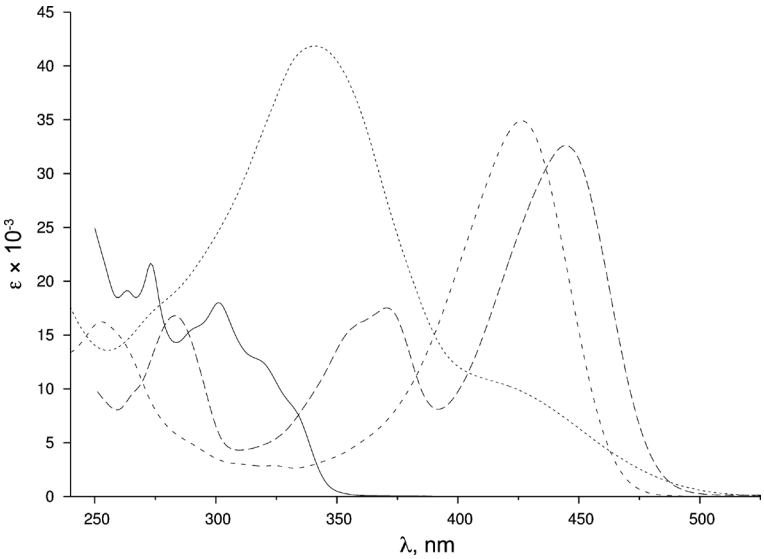


Fig. 1. Absorption spectra of coumarins at room temperature: **3** (solid line), **9** (short dash), **23** (dotted line) and **33** (dashed line)

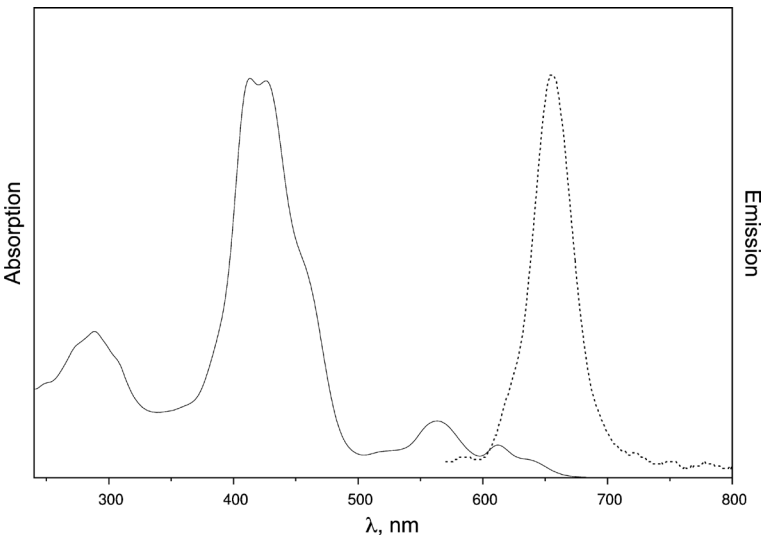


Fig. 2. Absorption and emission spectra of coumarin-corrole **18**

EXPERIMENTAL

General

All chemicals were used as received unless otherwise noted. Reagent grade solvents (MeCN, CH_2Cl_2, hexanes, 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 (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) [20] 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 the eluent. Mass spectra were obtained on AMD-604 (AMD Intectra GmbH), compounds **3**, **9**, **10**, **13**, **17**, **23**, **28**, **29**, **33** and **34**; Mariner (Perseptive Biosystems, Inc.), compounds **5**, **18**, **24** and **30**; 4000 Q-TRAP (Applied Biosystems), compounds **11** and **35**; GCT Premier (Waters), compounds **15** and **25**. The following compounds were prepared as described in the literature: **1** [21], **4** [22], **12** [23], **14** [19], **16** [24], **22** [25].

A Perkin-Elmer Lambda 25 UV-vis spectrophotometer and a Hitashi F7000 spectrofluorimeter were used to acquire absorption and emission spectra. Spectrophotometric grade solvents were used without further purification.

Synthesis

Preparation of 2,3,5,6-tetrafluoro-4-((6-oxo-6*H*-benzo[c]chromen-3-yl)oxy)-benzaldehyde (3). 3-hydroxy-6*H*-benzo[c]chromen-6-one (**1**, 1.06 g, 5 mmol) was dissolved in DMF (10 mL). Then cesium fluoride (1.52 g, 10 mmol) was added, followed by pentafluorobenzaldehyde **2** (0.62 mL, 5 mmol). A white precipitate was formed immediately after the aldehyde addition. The reaction was stirred for 2 h, diluted with water and stirred for further 30 min. The obtained precipitate was filtered off, washed thoroughly with water and air-dried. Crystallization from glacial acetic acid yielded compound **3** (1.67 g, 86%) as an off-white solid; R_f 0.6 (chloroform), mp 227–228 °C. Anal. calcd. for $C_{20}H_8F_4O_4$: C, 61.87; H, 2.08; F, 19.57%. Found: C, 61.98; H, 2.28; F, 19.57. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 263 (1.9), 273 (2.2), 301 (1.8). ^{1}H NMR (500 MHz; DMSO-d_6; Me_4Si): δ_H, ppm 7.32 (1H, dd, J_3 = 8.8 Hz, J_4 = 2.6 Hz, coum), 7.37 (1H, d, *J* = 2.6 Hz, coum), 7.69 (1H, m, coum), 7.97 (1H, m, coum), 8.25 (1H, m, coum), 8.43 (2H, m, coum), 10.24 (1H, s, C*H*O). ^{13}C NMR (125 MHz; DMSO-d_6; Me_4Si): δ_C, ppm 104.9, 112.4, 113.2, 114.9, 120.4, 123.1, 126.1, 129.2, 130.2, 134.4, 135.9, 137.1, 141.4 (dm, *J* = 235 Hz), 147.7 (dm, *J* = 250 Hz), 152.4, 157.9, 160.5, 183.9. HRMS (EI): *m/z* 388.0363 (calcd. for $[M]^+$ 388.0359).

Preparation of 5,15-bis(pentafluorophenyl)-10-(4-((6-oxo-6*H*-benzo[c]chromen-3-yl)oxy)-2,3,5,6-tetrafluorophen-1-yl)corrole (5). Aldehyde **3** (970 mg, 2.5 mmol) and 5-(pentafluorophenyl)dipyrromethane (**4**, 1.56 g, 5 mmol) were suspended in dichloromethane (37 mL). Then the pre-prepared solution of TFA (410 μL, TFA/dichloromethane 1:10) was added while stirring to

achieve a TFA concentration of 13.5 μM. The reaction was stirred at rt for 40 min and monitored by TLC (aldehyde consumption). After that, triethylamine (70 μL, 0.5 μmol) was added to quench the reaction. The resulting solution was diluted to 150 mL with dichloromethane and oxidised with DDQ (1.48 g, 6.5 mmol; dissolved in a minimal amount of toluene). After 2 h, the reaction mixture was filtered through a silica pad, corrole containing fractions were collected and evaporated with celite and then chromatographed on a 15 cm column, eluting with dichloromethane/hexanes (increasing polarity gradually from hexanes to dichloromethane/hexanes 1:1; when the red fluorescent product was close to the bottom of a column, 0.2% of methanol was added to the eluent). Crystalline sample was obtained by boiling collected product in a small amount of dichloromethane and filtering off precipitate after cooling the mixture, R_f 0.6 (dichloromethane/hexanes 2:1). Yield 150 mg (6%). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 274 (3.7), 301 (3.1), 408 (14.5), 562 (2.3), 604 (1.3). ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 7.35 (1H, dd, J_3 = 8.4 Hz, J_4 = 2.4 Hz, coum), 7.62 (1H, m, coum), 7.88 (1H, m, coum), 8.13 (1H, d, J = 8.4 Hz, coum), 8.20 (1H, d, J = 9.2 Hz, coum), 8.43 (1H, m, coum), 8.59 (2H, m, β-*H*-pyrrole), 8.69 (2H, d, J = 4.4 Hz, β-*H*-pyrrole), 8.82 (2H, d, J = 4.4 Hz, β-*H*-pyrrole), 9.12 (2H, d, J = 4.4 Hz, β-*H*-pyrrole); one signal from the coumarin moiety is hidden under the solvent peak. HRMS (ESI): *m/z* 989.1226 (calcd. for $[M + H]^+$ 989.1228).

Preparation of methyl 4′-(5,5-dimethyl-1,3-dioxan-2-yl)benzoylacetate (7). Activated zinc (13.08 g, 0.2 mol) was suspended in anh. boiling THF (120 mL). A few drops of methyl bromoacetate were added while reflux was maintained, followed by acetal **6** (8.68 g, 40 mmol). Subsequently, methyl bromoacetate was added (15 mL, 160 mmol, dropwise, over 30 min) and heating was continued for additional 15 min. Then, the reaction mixture was cooled to rt and HCl aq (10%, 40 mL) was slowly added. The resulting mixture was extracted a few times with CH_2Cl_2, and the organic extracts were washed with H_2O, dried with Na_2SO_4 and chromatographed (SiO_2, CH_2Cl_2, then CH_2Cl_2/acetone, 98:2, 95:5) to afford the expected ester **7** contaminated with small amounts of an unidentified compound that could not be removed by further chromatography. This material was used in the next step without any further purification.

Preparation of 3-[4-(5,5-dimethyl-1,3-dioxan-2-yl)-benzoyl]-7-diethylamino-2-oxo-2*H*-chromen (9). Ester **7** (1.5 g, 5 mmol, crude), 4-diethylamino-2-hydroxybenzaldehyde (**8**, 965 mg, 5 mmol) and pyrrolidine (200 μL, 2.4 mmol) were dissolved in MeOH (200 mL) and the resulting mixture was refluxed for 6 h. Subsequently, the reaction mixture was cooled to 4 °C, and the precipitate was filtered off and washed with cold MeOH to afford 1.07 g of the expected product. The supernatant was evaporated and chromatographed (SiO_2, CH_2Cl_2/acetone, 95:5) giving an additional 237 mg of coumarin **9**. The total yield was 1.31 g (60%). mp 175–176 °C. Anal. calcd. for $C_{26}H_{29}NO_5$: C, 71.70; H, 6.71; N, 3.22%. Found: C, 71.75; H, 6.82; N, 3.04. IR (KBr): ν, cm^{-1} 782, 1098, 1234, 1350, 1510, 1579, 1620, 1639, 1718, 1918. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 253 (1.6), 426 (3.5). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm 0.81 (3H, s, CH_3), 1.24 (6H, t, J = 7.1 Hz, 2 × CH_2CH_3), 1.29 (3H, s, CH_3), 3.45 (4H, q, J = 7.1 Hz, 2 × CH_2CH_3), 3.67 (2H, d, J = 11 Hz, CH_2O), 3.79 (2H, d, J = 11 Hz, CH_2O), 5.44 (1H, s, CH acetal), 6.50 (1H, d, J = 2.4 Hz, Ar), 6.61 (1H, dd, J_3 = 8.9 Hz, J_4 = 2.4 Hz, Ar), 7.32 (1H, d, J = 8.9 Hz, Ar), 7.59, 7.82 (2 × 2H, AA′BB′, J = 8.3 Hz, C_6H_4), 8.01 (1H, s, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 12.4, 21.8, 23.0, 30.2, 45.1, 77.6, 97.0, 100.9, 107.7, 109.6, 117.7, 126.0, 129.4, 130.9, 138.2, 142.6, 147.8, 152.6, 158.2, 159.4, 192.2. HRMS (EI): *m/z* 435.2035 (calcd. for $[M]^{+}$ 435.2046).

Preparation of 3-(4-formylbenzoyl)-7-diethylamino-2-oxo-2*H*-chromen (10). Acetal **9** (1.0 g, 2.3 mmol) was dissolved in CH_2Cl_2 (10 mL), TFA (5 mL) was slowly added, followed by H_2O (1 mL) and the resulting mixture was vigorously stirred for 48 h. Subsequently, the acid was neutralised with $NaHCO_3$ aq, the resulting suspension was extracted three times with CH_2Cl_2, the combined organic phases were washed with H_2O and dried (Na_2SO_4). The solvent was removed and the residue was crystallised from MeOH to afford 789 mg (98%) of coumarin **10**. An analytically pure sample was obtained by chromatography (SiO_2, CH_2Cl_2/acetone, 95:5). mp 123–124 °C. Anal. calcd. for $C_{21}H_{19}NO_4$: C, 72.19; H, 5.48; N, 4.01%. Found: C, 71.79; H, 5.35; N, 4.12. IR (KBr): ν, cm^{-1} 1231, 1352, 1511, 1579, 1619, 1706. UV-vis (toluene): λ_{max}, nm 432. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm 1.26 (6H, t, J = 7.1 Hz, 2 × CH_2CH_3), 3.47 (4H, q, J = 7.1 Hz, 2 × CH_2CH_3), 6.51 (1H, d, J = 2.4 Hz, Ar), 6.65 (1H, dd, J_3 = 9 Hz, J_4 = 2.4 Hz, Ar), 7.40 (1H, d, J = 9 Hz, Ar), 7.90, 7.97 (2 × 2H, AA′BB′, J = 8.4 Hz, C_6H_4), 8.23 (1H, s, CH), 10.09 (1H, s, CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 12.4, 45.2, 97.0, 108.1, 109.9, 116.6, 129.3, 129.4, 131.5, 138.4, 143.3, 148.7, 153.1, 158.7, 159.8, 191.7, 192.1. HRMS (EI): *m/z* 349.1325 (calcd. for $[M]^{+}$ 349.1314).

Preparation of corrole 11. 5-(pentafluorophenyl)-dipyrromethane (**4**, 625 mg, 2 mmol) and coumarin **10** (349 mg, 1 mmol) were dissolved in CH_2Cl_2 (60 mL) and TFA (230 μL, 3 mmol) was slowly added. After stirring at rt for 1 h, Et_3N (416 μL, 3 mmol) was added. DDQ (1590 mg, 2.6 mmol) was dissolved in toluene/CH_2Cl_2 (1:5, 60 mL) and both solutions were added simultaneously *via* syringes to vigorously stirred CH_2Cl_2 (50 mL). After 15 min, the reaction mixture was concentrated to one quarter of the initial volume and filtered through a short (5 cm) silica pad (CH_2Cl_2, then CH_2Cl_2/acetone, 98:2). The fluorescent band was collected, evaporated and rechromatographed (DCVC, SiO_2, CH_2Cl_2, then CH_2Cl_2/acetone, 98:2). Crystallization from $CHCl_3$/hexane gave 88 mg (9%) of corrole **11**. R_f 0.42 (CH_2Cl_2/acetone, 98:2). Anal. calcd. for $C_{51}H_{28}F_{10}N_5O_3$: C, 64.49; H, 3.08;

N, 7.37%. Found: C, 64.65; H, 2.79; N, 7.15. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 298 (2.1), 421 (13.1), 563 (1.6), 612 (1.3). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm (-5)-(-1) (3H, br s), 1.27 (6H, t, J = 7.1 Hz, 2 × CH_2CH_3), 3.48 (4H, q, J = 7.1 Hz, 2 × CH_2CH_3), 6.56 (1H, d, J = 2.3 Hz, Ar), 6.65 (1H, dd, J_3 = 9 Hz, J_4 = 2.3 Hz, Ar), 7.47 (1H, d, J = 9 Hz, Ar), 8.20, 8.27 (2 × 2H, AA′BB′, J = 8.4 Hz, C_6H_4), 8.3 (1H, s, CH), 8.57 (2H, br s, β-H), 8.72 (2H, d, J = 4.6 Hz, β-H), 8.75 (2H, d, J = 4.6 Hz, β-H), 9.11 (2H, d, J = 4.1 Hz, β-H). MS (ESI): *m/z* 950.4 (calcd. for $[M + H]^+$ 950.2).

Preparation of 6-bromo-7-diethylamino-3-methoxycarbonyl-2-oxo-2*H*-chromen (13). Aldehyde **12** (1.48 g, 5.4 mmol), dimethyl malonate (621 μL, 5.4 mmol), pyrrolidine (40 μL, 0.48 mmol) and AcOH (30 μL, 0.48 mmol) were dissolved in hot MeOH (10 mL) and the resulting mixture was heated under reflux for 6 h. Subsequently, the reaction mixture was cooled to 4 °C, and the precipitate was filtered off and washed with cold MeOH to afford 1.74 g (90%) of yellow crystals. mp 99–100 °C. Anal. calcd. for $C_{15}H_{16}NO_4Br$: C, 50.86; H, 4.55; N, 3.95%. Found: C, 51.03; H, 4.46; N, 3.68. IR (KBr): ν, cm^{-1} 793, 1218, 1598, 1691, 1708, 1747. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 397 (2.2). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm 1.15 (6H, t, J = 7.0 Hz, 2 × CH_2CH_3), 3.32 (4H, q, J = 7.0 Hz, 2 × CH_2CH_3), 3.94 (3H, s, CO_2CH_3), 6.88 (1H, s, Ar), 7.75 (1H, s, Ar), 8.42 (1H, s, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 12.3, 46.0, 52.7, 108.7, 112.9, 113.6, 114.3, 134.4, 148.0, 155.3, 155.6, 156.8, 163.9. HRMS (EI): *m/z* 353.0269 (calcd. for $[M]^{+}$ 353.0263).

Preparation of corrole 15. Corrole **14** (48 mg, 65 μmol), coumarin **13** (23 mg, 65 μmol), Cs_2CO_3 (23 mg, 70 μmol), $Pd(OAc)_2$ (0.67 mg, 3.3 μmol) and PPh_3 (3.1 mg, 13.2 μmol) were placed in a Schlenk tube and anh. DMSO (2 mL) was added under an argon atmosphere. After heating at 80 °C for 24 h, the solvent was removed under reduced pressure and the residue was chromatographed (SiO_2, CH_2Cl_2, then CH_2Cl_2/acetone 98:2). Fractions containing the expected product were collected, evaporated and further purified using SEC (THF). Crystallisation from $CHCl_3$/hexanes gave 31 mg of corrole **15** (52%). R_f 0.27 (CH_2Cl_2/acetone 98:2). Anal. calcd. for $C_{54}H_{31}F_{10}N_5O_4 \times 2H_2O$: C, 62.37; H, 3.39; N, 6.73%. Found: C, 62.09; H, 3.29; N, 6.43. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 292 (3.4), 422 (14), 563 (1.5), 614 (1.3). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm (-4)-(-1.5) (3H, br s, NH), 1.44 (6H, t, J = 7.0 Hz, 2 × CH_2CH_3), 3.82 (4H, q, J = 7.0 Hz, 2 × CH_2CH_3), 3.93 (3H, s, CO_2CH_3), 6.70 (1H, s, Ar), 7.81 (1H, s, Ar), 7.90, 8.21 (2 × 2H, AA'BB', J = 7.9 Hz, C_6H_4), 8.47 (1H, s, CH). 8.58 (2H, br s, β-H), 8.73 (4H, br s, β-H), 9.12 (2H, br s, β-H). MS (FD): *m/z* 1003.2 (calcd. for $[M]^{+}$ 1003.2).

Preparation of 6-bromo-3-[(7-diethylamino-2-oxo-2*H*-chromen-3-yl)carbonyl]-4a,8a-dihydro-2*H*-chromen-2-on (17). 5-bromosalicylaldehyde (100 mg, 0.5 mmol), ester **16** (159 mg, 0.5 mmol), pyrrolidine (50 μL, 0.6 mmol) and AcOH (35 μL, 0.6 mmol) were dissolved in hot MeOH (50 mL) and the resulting mixture was heated under reflux for 6 h. Subsequently, the reaction mixture was cooled to 4 °C, and the precipitate was filtered off and washed with cold MeOH to afford 188 mg of **17** (80%). mp 268–269 °C. Anal. calcd. for $C_{23}H_{18}NO_5Br$: C, 58.99; H, 3.87; N, 2.99%. Found: C, 58.86; H, 3.99; N, 3.04. IR (KBr): ν, cm^{-1} 1505, 1572, 1608, 1711, 1730. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 430 (5.8). ^{1}H NMR (500 MHz, DMSO-d_6): δ_H, ppm 1.16 (6H, t, J = 6.9 Hz, 2 × CH_2CH_3), 3.28 (4H, q, J = 6.9 Hz, 2 × CH_2CH_3), 6.63 (1H, d, J = 2.1 Hz, Ar), 6.85 (1H, dd, J_3 = 9.0 Hz, J_4 = 2.1 Hz, Ar), 7.47 (1H, d, J = 8.8 Hz, Ar), 7.72 (1H, d, J = 9.0 Hz, Ar), 7.87 (1H, dd, J_3 = 8.8 Hz, J_4 = 2.3 Hz, Ar), 8.13 (1H, d, J = 2.3 Hz, Ar), 8.27 (1H, s, CH), 8.57 (1H, s, CH). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C, ppm 12.3, 44.5, 96.2, 107.7, 110.4, 115.1, 116.4, 118.5, 120.3, 130.2, 131.5, 132.6, 135.4, 141.0, 147.7, 152.7, 153.3, 157.8, 158.2, 159.8, 186.6. HRMS (EI): *m/z* 467.0360 (calcd. for $[M]^{+}$ 467.0368).

Preparation of corrole 18. Corrole **14** (72 mg, 100 μmol), coumarin **17** (56 mg, 120 μmol), Cs_2CO_3 (27.6 mg, 104 μmol), $Pd(OAc)_2$ (5.0 mg, 25 μmol) and PPh_3 (24 mg, 100 μmol) were placed in Schlenk tube and anh. DMSO (2 mL) was added under an argon atmosphere. After heating at 80 °C for 24 h, the solvent was removed under reduced pressure and the residue was chromatographed (SiO_2, CH_2Cl_2, then CH_2Cl_2/acetone 98:2). Fractions containing the expected product were collected, evaporated and further purified using SEC (THF). Crystallization from $CHCl_3$/hexanes gave 62 mg of corrole **18** (55%). R_f 0.45 (CH_2Cl_2). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 289 (5.3), 413 (14.5), 426 (14.5), 563 (2.0), 612 (1.2). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm (-4)-(-1.5) (3H, br s, NH), 1.25 (6H, t, J = 7.1 Hz, 2 × CH_2CH_3), 3.48 (4H, q, J = 7.1 Hz, 2 × CH_2CH_3), 6.49 (1H, d, J = 2.2 Hz, Ar), 6.63 (1H, dd, J_3 = 9 Hz, J_4 = 2.2 Hz, Ar), 7.42 (1H, d, J = 8.5 Hz, Ar), 7.43 (1H, d, J = 9 Hz, Ar), 7.85 (1H, dd, J_3 = 8.5 Hz, J_4 = 1.9 Hz, Ar), 7.88 (1H, d, J = 1.9 Hz, Ar), 7.98, 8.21 (2 × 2H, AA′BB′, J = 7.8 Hz, C_6H_4), 8.02 (1H, s, Ar), 8.34 (1H, s, CH), 8.59 (2H, br s, β-H), 8.75 (4H, br s, β-H), 9.12 (2H, br d, J = 3.2 Hz, β-H). MS (ESI): *m/z* 1118.2 (calcd. for $[M + H]^+$ 1118.2).

Preparation of 4-[(4′-formylbiphenyl-4)-ethenyl]-7-diethylamino-2-oxo-2*H*-chromen (23). A mixture of coumarin **19** (925 mg, 4 mmol) and *tert*-BuOK (449 mg, 4 mmol) in DMSO (10 mL) was stirred for 10 min. Aldehyde **21** (1.11 g, 5 mmol) was added and the resulting mixture was stirred at rt for 5 h. Subsequently, AcOH (1.5 mL) was added, followed by water (90 mL). A yellow-red precipitate appeared, which was filtered off, washed with water and air dried. Chromatography on silica (CH_2Cl_2, then CH_2Cl_2/acetone 95:5) followed by crystallization from EtOH afforded 461 mg (27%) of **23** (contaminated with some unidentified species) as red crystals. mp 180 °C (dec.). Anal. calcd. for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N, 3.31%. Found: C, 79.22; H, 5.73;

N, 3.28. IR (KBr): ν, cm^{-1} 813, 1138, 1412, 1520, 1604, 1696. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 341 (4.2). ^1H NMR (500 MHz, $CDCl_3$): δ_H, ppm 1.15 (6H, t, J = 7.1 Hz, 2 × CH_2CH_3), 3.46 (4H, q, J = 7.1 Hz, 2 × CH_2CH_3), 6.39 (1H, s, CH), 6.56 (1H, d, J = 2.6 Hz, Ar), 6.72 (1H, dd, J_3 = 9.0 Hz, J_4 = 2.6 Hz, Ar), 7.65 (1H, d, J = 16 Hz, CH=CH), 7.72 (1H, d, J = 16 Hz, CH=CH), 7.87 (1H, d, J = 9 Hz, Ar), 7.93–8.03 (8H, m, biphenyl), 10.07 (1H, s, CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 12.8, 44.4, 97.6, 102.4, 107.3, 109.0, 121.8, 126.8, 127.7, 127.9, 128.4, 129.1, 130.6, 135.7, 136.7, 139.6, 145.5, 150.4, 150.9, 156.6, 161.6, 193.152. HRMS (EI): 423.1853 (calcd. for $[M]^+$ 423.1834).

Preparation of corrole 24. 5-(pentafluorophenyl)-dipyrromethane (**4**, 250 mg, 0.8 mmol) and coumarin **22** (139 mg, 0.4 mmol) were dissolved in CH_2Cl_2 (24 mL) and TFA (96 μL, 1.2 mmol) was slowly added. After stirring at rt for 1 h, Et_3N (166 μL, 1.2 mmol) was added and the reaction mixture was diluted by adding of 600 mL of CH_2Cl_2. Subsequently, DDQ (236 mg, 1.04 mmol) in THF (1.5 mL) was added with vigorous stirring. After 15 min, the reaction mixture was concentrated to 50 mL and filtered through a short (5 cm) silica pad (CH_2Cl_2, then CH_2Cl_2/acetone, 95:5). The fluorescent band was collected, evaporated and rechromatographed (DCVC, SiO_2, CH_2Cl_2, then CH_2Cl_2/acetone, 95:5). Crystallization from $CHCl_3$/hexanes gave 63 mg (17%) of corrole **24**. R_f 0.64 (CH_2Cl_2/acetone, 95:5). Anal. calcd. for $C_{52}H_{31}F_{10}N_5O_2$: C, 65.89; H, 3.30; N, 7.39%. Found: C, 65.98; H, 3.13; N, 7.29. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 305 (3.7), 413 (41.7), 563 (2.2), 612 (1.3). ^1H NMR (500 MHz, $CDCl_3$): δ_H, ppm (-4)-(-1.5) (3H, br s, NH), 1.25 (6H, t, J = 7.1 Hz, 2 × CH_2CH_3), 3.45 (4H, q, 7.1 Hz, 2 × CH_2CH_3), 6.38 (1H, s, CH), 6.57 (1H, d, J = 2.6 Hz, Ar), 6.66 (1H, dd, J_3 = 9.0 Hz, J_4 = 2.6 Hz, Ar), 7.60 (2H, br s, C*H*=C*H*), 7.71 (1H, d, J = 9 Hz, Ar), 7.97, 8.24 (2 × 2H, AA′BB′, J = 7.9 Hz, C_6H_4), 8.58 (2H, br d, J = 2.6 Hz, β-H), 8.74 (4H, br s, β-H), 9.12 (2H, d, J = 4.1 Hz, β-H). HRMS (ESI): *m/z* 948.2421 (calcd. for $[M + H]^+$ 948.2391).

Preparation of corrole 25. 5-(pentafluorophenyl)-dipyrromethane (**4**, 500 mg, 1.6 mmol) and coumarin **23** (339 mg, 0.8 mmol) were dissolved in CH_2Cl_2 (48 mL) and TFA (192 μL, 2.4 mmol) was slowly added. After stirring at rt for 1 h, Et_3N (332 μL, 2.4 mmol) was added. DDQ (472 mg, 2.08 mmol) was dissolved in toluene/CH_2Cl_2 (1:2, 48 mL) and both solutions were added simultaneously *via* syringes to vigorously stirred CH_2Cl_2 (50 mL). After 15 min, the reaction mixture was concentrated to one quarter of the initial volume and filtered through a short (10 cm) silica pad (CH_2Cl_2, then CH_2Cl_2/acetone, 99:1). The fluorescent band was collected, evaporated and loaded on SEC (THF). Fractions containing the desired product were evaporated to afford 10 mg (1.2%) of corrole **25**. R_f 0.59 (CH_2Cl_2/acetone, 95:5). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 347 (3.8), 413 (11.2), 562 (1.6), 613 (0.9). ^1H NMR (500 MHz, $CDCl_3$): δ_H, ppm (-4)-(-1.5) (3H, br s, NH), 1.25 (6H, t, J = 7.2 Hz, 2 × CH_2CH_3), 3.45 (4H, q, 7.2 Hz, 2 × CH_2CH_3), 6.32 (1H, s, CH), 6.57 (1H, d, J = 2.6 Hz, Ar), 6.65 (1H, dd, J_3 = 9.0 Hz, J_4 = 2.6 Hz, Ar), 7.43 (2H, br s, C*H*=C*H*), 7.65 (1H, d, J = 9 Hz, Ar), 7.79, 7.97 (2 × 2H, AA′BB′, J = 8.4 Hz, C_6H_4), 8.04, 8.29 (2 × 2H, AA′BB′, J = 8.0 Hz, C_6H_4), 8.59 (2H, d, J = 4.2 Hz, β-H), 8.74 (2H, d, J = 4.6 Hz, β-H), 8.80 (2H, d, J = 4.6 Hz, β-H), 9.13 (2H, d, J = 4.2 Hz, β-H). MS (FD): *m/z* 1023.2 (calcd. for $[M]^+$ 1023.3).

Preparation of 4-[(4-trifluoromethylphenyl)-ethenyl]-7-hydroxy-2-oxo-2*H*-chromen (28). A mixture of coumarin **26** (3.52 g, 20 mmol) and *tert*-BuOK (4.49 g, 40 mmol) in DMSO (80 mL) was stirred for 10 min. Aldehyde **27** (4.1 mL, 30 mmol) was added and the resulting mixture was stirred at rt for 5 h. Subsequently, AcOH (10 mL) was added, followed by water (400 mL). A yellow-red precipitate appeared, which was filtered off, washed with water and air dried. Crystallization from EtOH afforded 2.6 g (39%) of **28** as yellowish crystals. mp 259–261 °C. Anal. calcd. for $C_{18}H_{11}O_3F_3$: C, 65.06; H, 3.34%. Found: C, 64.83; H, 3.16. IR (KBr): δ, cm^{-1} 842, 1066, 1321, 1386, 1677, 3103. UV-vis (CH_3CN): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 308 (2.2). ^1H NMR (500 MHz, DMSO-d_6): δ_H, ppm 6.57 (1H, s, CH), 6.74 (1H, d, J = 2.3 Hz, Ar), 6.82 (1H, dd, J_3 = 8.7 Hz, J_4 = 2.5 Hz, Ar), 7.66 (1H, d, J = 16 Hz, CH=CH), 7.76–7.80 (3H, m, CH=CH + C_6H_4), 8.00 (2H, d, J = 7.8 Hz, C_6H_4), 8.02 (1H, d, J = 9 Hz, Ar), 10.59 (1H, s, OH). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C, ppm 103.0, 106.2, 111.0, 113.4, 123.9, 126.0 (q, J = 2.7 Hz), 127.2, 128.9, 129.4 (q, J = 38 Hz), 136.3, 140.30, 14.31, 150.2, 155.8, 161.1, 161.8. HRMS (EI): *m/z* 332.0667 (calcd. for $[M]^+$ 332.0660).

Preparation of aldehyde 29. A mixture of coumarin **28** (664 mg, 2 mmol), aldehyde **2** (248 μL, 2 mmol) and CsF (608 mg, 4 mmol) in DMF (10 mL) was stirred at 65 °C for 1 h. Subsequently, water was added and the resulting mixture was extracted with CH_2Cl_2. The organic solvent was removed under reduced pressure and the residue was crystallized from EtOH to afford 800 mg (79%) of **29** as off-white crystals. mp 236–239 °C. Anal. calcd. for $C_{25}H_{11}O_4F_7$: C, 59.07; H, 2.18%. Found: C, 59.08; H, 1.96. IR (KBr): ν, cm^{-1} 841, 1114, 1327, 1489, 1613, 1698. UV-vis (DMSO): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 315 (2.5). ^1H NMR (500 MHz, DMSO-d_6): δ_H, ppm 6.82 (1H, s, CH), 7.32 (1H, dd, J_3 = 9.0 Hz, J_4 = 2.8 Hz, Ar), 7.37 (1H, d, J = 2.8 Hz, Ar), 7.75 (1H, d, J = 16 Hz, CH=CH), 7.82, 8.05 (2 × 2H, AA′BB′, J = 8.2 Hz, C_6H_4), 7.87 (1H, d, J = 16 Hz, CH=CH), 8.31 (1H, d, J = 9.0 Hz, Ar), 10.24 (1H, s, CHO). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C, ppm 104.3, 109.3, 112.7 (m), 113.0, 1115.4, 123.4, 123.5, 126.1 (q, J = 3.9 Hz), 127.9, 128.0, 129.0, 129.7 (q, J = 38 Hz), 137.0 (m), 140.2 (m), 146.6 (m), 148.7 (m), 149.6, 155.3, 159.0, 160.4, 183.9. HRMS (EI): *m/z* 508.0539 (calcd. for $[M]^+$ 508.0546).

Preparation of corrole (30). 5-(pentafluorophenyl)-dipyrromethane (**4**, 375 mg, 1.2 mmol) and coumarin **29** (306 mg, 0.6 mmol) were dissolved in CH_2Cl_2 (18 mL) and TFA (18 μL, 0.23 mmol) was slowly added. After

stirring at rt for 1 h (coumarin slowly dissolved), Et_3N (33 μL, 0.23 mmol) was added. DDQ (354 mg, 1.56 mmol) was dissolved in toluene/CH_2Cl_2 (1:2, 18 mL) and both solutions were added simultaneously *via* syringes to vigorously stirred CH_2Cl_2 (40 mL). After 15 min, the reaction mixture was concentrated to one quarter of the initial volume and filtered through a short (10 cm) silica pad (CH_2Cl_2/hexanes, 1:1). The fluorescent band was collected, evaporated and loaded on SEC (THF). Fractions containing the desired product were evaporated to afford 33 mg (5%) of corrole **30**. R_f 0.33 (CH_2Cl_2/hexane, 3:1). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 308 (4.2), 408 (12.3), 562 (2.0), 604 (1.1). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm (-4)-(-1.5) (3H, br s, NH), 6.59 (1H, s, CH), 7.24 (1H, d, J = 2.0 Hz, Ar), 7.33 (1H, dd, J_3 = 9.0 Hz, J_4 = 2.0 Hz, Ar), 7.38 (1H, d, J = 16 Hz, C*H*=C*H*), 7.46 (1H, d, J = 16 Hz, C*H*=C*H*), 7.72 (4H, br s, C_6H_4), 7.92 (1H, d, J = 9 Hz, Ar), 8.04, 8.29 (2 × 2H, AA′BB′, J = 8.0 Hz, C_6H_4), 8.54 (2H, br s, β-H), 8.70 (2H, d, J = 4.5 Hz, β-H), 8.82 (2H, d, J = 4.5 Hz, β-H), 9.08 (2H, br s, β-H). HRMS (ESI): *m/z* 1109.1372 (calcd. for $[M + H]^+$ 1109.1415).

Preparation of 3-(diethylamino)-10-hydroxychromeno[3,4-c]chromene-6,7-dione (33). 7-hydroxycoumarin-3-carboxylic acid ethyl ester (**31**, 2.34 g, 10 mmol) was heated together with *m*-diethylaminophenole (**32**, 1.65 g, 10 mmol) at 140 °C for 6 h. After cooling, the reaction mixture was triturated with diethyl ether to wash out unreacted material and other contaminants, after which dark orange crystals appeared. Precipitate was collected by filtration and the crude product was boiled in isopropanol, then filtered after cooling and air-dried. Yield 965 mg (55%); mp 281–283 °C. R_f 0.5 (dichloromethane/acetone 7:3). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 283 (1.7), 371 (1.7), 444 (3.2). ^{1}H NMR (600 MHz; DMSO-d_6; Me_4Si): δ_H, ppm 1.17 (6H, t, J = 6.9 Hz, CH_3), 3.50 (4H, q, J = 7.0 Hz, CH_2), 6.55 (1H, d, J = 3.0 Hz, Ar), 6.72 (1H, d, J = 3.0 Hz, Ar), 6.80 (1H, dd, J_3 = 9.6 Hz, J_4 = 2.4 Hz, Ar), 6.89 (1H, dd, J_3 = 9.3 Hz, J_4 = 2.7 Hz, Ar), 8.07 (1H, d, J = 9.6 Hz, Ar), 8.15 (1H, d, J = 9.0 Hz, Ar), 11.07 (1H, br s, hydroxyl). ^{13}C NMR (150 MHz; DMSO-d_6; Me_4Si): δ_C, ppm 12.8, 44.7, 97.0, 97.2, 103.2, 103.7, 108.0, 110.2, 114.0, 130.9, 131.4, 152.3, 152.8, 156.4, 156.7, 157.0, 157.9, 163.8. HRMS (EI): *m/z* 351.1096 (calcd. for $[M]^+$ 351.1107).

Preparation of 4-((10-(diethylamino)-6,7-dioxo-6,7-dihydrochromeno[3,4-c]chromen-3-yl)oxy)-2,3,5,6-tetrafluorobenzaldehyde (34). Compound **33** (878 mg, 2.5 mmol) was dissolved in DMF (5 mL). Then cesium fluoride (760 mg, 5 mmol) was added, followed by pentafluorobenzaldehyde (**2**, 310 μL, 2.5 mmol). After stirring for 2 h, the reaction mixture was diluted with water and stirring was continued for a further 30 min. After that, the reaction mixture was extracted with dichloromethane. The organic fractions were combined, washed with water, brine and dried over $MgSO_4$. After filtration, celite was added and the solvent was removed under reduced pressure. The product was chromatographed on a short column eluting with 1% methanol in dichloromethane; R_f 0.45 (dichloromethane/methanol 95:5). The product-containing fractions were collected, dried and crystallized from chloroform/hexane, yielding the title compound (895 mg, 68%) as a yellow solid; mp 240–241 °C. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 291 (2.7), 345 (1.5), 460 (3.2). ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 1.28 (6H, t, J = 7.2 Hz, CH_3), 3.50 (4H, q, J = 7.2 Hz, CH_2), 6.52 (1H, d, J = 2.7 Hz, Ar), 6.71 (1H, dd, J_3 = 9.4 Hz, J_4 = 2.7 Hz, Ar), 6.94 (1H, d, J = 2.7 Hz, Ar), 7.05 (1H, dd, J_3 = 9.1 Hz, J_4 = 2.7 Hz, Ar), 8.00 (1H, d, J = 9.4 Hz, Ar), 8.26 (1H, d, J = 9.1 Hz, Ar), 10.34 (1H, s, formyl). ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): δ_C, ppm 12.7, 45.4, 98.0, 99.3, 104.1, 104.8, 110.1, 112.5, 112.9, 130.1, 131.0, 151.8, 153.2, 156.4, 156.8, 157.2, 158.5, 160.1, 181.9. HRMS (EI): *m/z* 527.0985 (calcd. for $[M]^+$ 527.0992).

Preparation of 5,15-bis(pentafluorophenyl)-10-(4-((10-(diethylamino)-6,7-dioxo-6,7-dihydrochromeno[3,4-c]chromen-3-yl)oxy)-2,3,5,6-tetrafluorophen-1-yl)corrole (35). Aldehyde **34** (370 mg, 0.7 mmol) and 5-(pentafluorophenyl)dipyrromethane (**4**, 440 mg, 1.4 mmol) were suspended in dichloromethane (10 mL). A pre-prepared solution of TFA in CH_2Cl_2 (230 μL, TFA/CH_2Cl_2 1:10) was added to this suspension to achieve a final TFA concentration *ca.* 2.7 μM. The progress of the reaction was monitored by TLC (aldehyde consumption); during the reaction, substrates gradually dissolved. After stirring the reaction for 40 min it was quenched by the addition of triethylamine (40 μL, 0.287 μmol). The resulting solution was diluted to 100 mL with dichloromethane and oxidized with DDQ (413 mg, 1.82 mmol; dissolved in minimal amount of toluene prior addition). After 2 h, the reaction mixture was filtered through a silica pad, evaporated with celite and chromatographed eluting with toluene/acetone 4:1; R_f 0.42. Yield 76 mg (10%). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-4}$) 291 (2.4), 408 (10.5), 459 (2.0), 562 (1.6), 604 (0.9). ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 1.30 (6H, t, J = 7.1 Hz, CH_3), 3.51 (4H, q, J = 7.1 Hz, CH_2), 6.57 (1H, d, J = 2.6 Hz, coum), 6.75 (1H, dd, J_3 = 9.4 Hz, J_4 = 2.6 Hz, coum), 7.22 (1H, d, J = 1.1 Hz, coum), 7.37 (1H, dd, J_3 = 9.1 Hz, J_4 = 2.5 Hz, coum), 8.11 (1H, d, J = 4.7 Hz, coum), 8.40 (1H, d, J = 4.5 Hz, coum), 8.59 (2H, br s, β-*H*-pyrrole), 8.69 (2H, d, J = 2.1 Hz, β-*H*-pyrrole), 8.83 (2H, d, J = 2.1 Hz, β-*H*-pyrrole), 9.12 (2H, d, J = 2 Hz, β-*H*-pyrrole). MS (ESI): *m/z* 1150.3 (calcd. for $[M + Na]^+$ 1150.2).

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 either in a one-pot synthesis from dipyrromethanes and formyl-coumarins or *via* Sonogashira coupling of ethynylcorroles with halogenocoumarins. The competitive Michael addition of dipyrromethanes to the α,β-unsaturated system of

coumarin most probably diminished the yield of corroles. Copper-free Sonogashira coupling can be used for the construction of bis-coumarin-corrole dyads. The spectroscopic properties of all dyads studied suggest that the components are weakly electronically coupled.

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REFERENCES

1. a) Paolesse R. In *The Porphyrin Handbook*, Vol. 2, Kadish KM, Smith KM and Guilard R. (Eds.) Academic Press: San Diego, CA, 2000; pp 201. b) Sessler JL and Weghorn SJ. In *Expanded, Contracted & Isomeric Porphyrins*, Pergamon: Oxford, 1997; pp 11. c) Erben C, Will S and Kadish KM. In *Porphyrin Handbook*, Vol. 2, Kadish KM, Smith KM and Guilard R. (Eds.) Academic Press: San Diego, CA, 2000; pp 233. d) Montforts FP, Glasenapp-Breiling M and Kusch D. In *Houben-Weyl Methods of Organic Chemistry*, Vol E9d, Schaumann E. (Ed.) Thieme: Stuttgart, New York, 1998; pp 665–672. e) Gryko DT. *Eur. J. Org. Chem*. 2002; 1735–1743. f) Guilard R, Kadish KM, Barbe J-M and Stern C. In *The Porphyrin Handbook*, Vol. 18, Kadish KM, Smith KM and Guilard R. (Eds.) Academic Press: 2003; pp 303–351. g) Gryko DT, Fox JP and Goldberg DP. *J. Porphyrins Phthalocyanines* 2004; **8**: 1091–1105. h) Nardis S, Monti D and Paolesse R. *Mini-Rev. Org. Chem*. 2005; **2**: 355–372. i) Goldberg DP. *Acc. Chem. Res*. 2007; **40**: 626–634. j) Aviv I and Gross Z. *Chem. Commun*. 2007; 1987–1999.
2. Johnson AW and Kay IT. *Proc. Chem. Soc. London*, 1964; 89–90.
3. a) Gross Z, Galili N and Saltsman I. *Angew. Chem. Int. Ed.* 1999; **38**: 1427–1429. b) Paolesse R, Nardis S, Sagone F and Khoury RM. *J. Org. Chem*. 2001; **66**: 550–556. c) Briñas RP and Brückner C. *Synlett* 2001; 442–444. d) Gryko DT and Jadach K. *J. Org. Chem*. 2001; **66**: 4267–4275. e) Barbe JM, Burdet F, Espinoza E, Gros CP and Guilard R. *J. Porphyrins Phthalocyanines* 2003; **7**: 365–374. f) Gryko DT, Tasior M and Koszarna B. *J. Porphyrins Phthalocyanines* 2003; **7**: 239–248. g) Geier GR III, Chick JFB, Callinan JB, Reid CG and Auguscinski WP. *J. Org. Chem.* 2004; **69**: 4159–4169. h) Jeandon C, Ruppert R and Callot HJ. *Chem. Commun*. 2004; 1090–1091. i) Koszarna B and Gryko DT. *J. Org. Chem*. 2006; **71**: 3707–3717.
4. Shao J, Shen J, Ou Z, Wenbo E, Koszarna B, Gryko DT and Kadish KM. *Inorg. Chem*. 2006; **45**: 2251–2265.
5. a) Ventura B, Degli Esposti A, Koszarna B, Gryko DT and Flamigni L. *New J. Chem*. 2005; **29**: 1559–1566. b) Ding T, Alemán EA, Mordarelli DA and Ziegler CJ. *J. Phys. Chem. A* 2005; **109**: 7411–7417. c) Kowalska D, Liu X, Tripathy U, Mahammed A, Gross Z, Hirayama S and Steer RP. *Inorg. Chem.* 2009; **48**: 2670–2676. d) Flamigni L and Gryko DT. *Chem. Soc. Rev*. 2009; **38**: 1635–1646.
6. a) Flamigni L, Ventura B, Tasior M and Gryko DT. *Inorg. Chim. Acta* 2007; **360**: 803–813. b) Tasior M, Gryko DT, Cembor M, Jaworski JS, Ventura B and Flamigni L. *New J. Chem*. 2007; **31**: 247–259. c) Flamigni L, Ventura B, Tasior M, Becherer T, Langhals H and Gryko DT. *Chem. Eur. J*. 2008; **14**: 169–183. d) Gros CP, Brisach F, Meristoudi A, Espinoza E, Guilard R and Harvey PD. *Inorg. Chem*. 2007; **46**: 125–135. e) Tasior M, Gryko DT, Shen J, Kadish KM, Becherer T, Langhals H, Ventura B and Flamigni L. *J. Phys. Chem. C* 2008; **112**: 19699–19709. f) D'Souza F, Chitta R, Ohkubo K, Tasior M, Subbaiyan NK, Zandler ME, Rogacki MK, Gryko DT and Fukuzumi S. *J. Am. Chem. Soc.* 2008; **130**: 14263–14272.
7. a) Alemayehu AB and Ghosh A. *J. Porphyrins Phthalocyanines* 2011; **15**: 106–110. b) McGown AJ, Kerber WD, Fujii H and Goldberg DP. *J. Am. Chem. Soc*. 2009; **131**: 8040–8048. c) Schöfberger W, Lengwin F, Reith LM, List M and Knör G. *Inorg. Chem. Commun*. 2010; **13**: 1187–1190. d) Reith LM, Himmelsbach M, Schöfberger W and Knör G. *J. Photochem. Photobiol. A* 2011; **218**: 247–253. e) Ramdhanie B, Stern CL and Goldberg DP. *J. Am. Chem. Soc*. 2001; **123**: 9447–9448. f) Gross Z. *J. Biol. Inorg. Chem*. 2001; **6**: 733–738. g) Alemayehu AB, Gonzalez E, Hansen LK and Ghosh A. *Inorg. Chem*. 2009; **48**: 7794–7799. h) Albrett, AM, Conradie J, Boyd PDW, Clark GR, Ghosh A and Brothers PJ. *J. Am. Chem. Soc*. 2008; **130**: 2888–2889. i) Bröring M, Brégier F, Tejero EC, Hell C and Holthausen MC. *Angew. Chem. Int. Ed*. 2007; **46**: 445–448. *Angew. Chem*. 2007; **119**: 449–452. j) Mody VV, Fitzpatrick MB, Zabaneh SS, Czernuszewicz RS, Gałęzowski M and Gryko DT. *J. Porphyrins Phthalocyanines* 2009; **13**: 1040–1052. k) Palmer HJ, Durrell AC, Gross Z, Winkler JR and Gray HB. *J. Am. Chem. Soc*. 2010; **132**: 9230–9231. k) Cho K, Kerber WD, Lee SR, Wan A, Batteas JD and Goldberg DP. *Inorg. Chem*. 2010; **49**: 8465–8473.
8. a) Stefanelli M, Nardis S, Tortora, L, Fronczek FR, Smith KM, Licoccia S and Paolesse R. *Chem. Commun*. 2011; **47**: 4255–4257. b) Tortora, L, Nardis S, Fronczek FR, Smith KM and Paolesse R. *Chem. Commun*. 2011; **47**: 4243–4245. c) Barata JFB, Silva AMG, Neves MGPMS, Tomé AC, Silva AMS and Cavaleiro JAS. *Tetrahedron Lett*. 2006; **47**: 8171–8174. d) Mahammed A and Gross Z. *J. Porphyrins Phthalocyanines* 2010; **14**: 911–923. e) Saltsman I, Mahammed A, Goldberg I, Tkachenko E,

Botoshansky M and Gross Z. *J. Am. Chem. Soc*. 2002; **124**: 7411–7420.
9. a) Kupershmidt L, Okun Z, Amit T, Mandel S, Saltsman I, Mahammed A, Bar-Am O, Gross Z and Youdim MBH. *J. Neurochem.* 2010; **113**: 363–373. b) Kanamori A, Catrinescu M-M, Mahammed A, Gross Z and Levin LA. *J. Neurochem.* 2010; **114**: 488–498.
10. Gryko DT. *J. Porphyrins Phthalocyanines* 2008; **12**: 906–917.
11. a) *The Chemistry of Heterocyclic Compounds, Volume 31, Chromenes, Chromanones, and Chromones*, Ellis GP. (Ed.) Wiley, John & Sons. b) Drexhage KH. In *Dye Lasers*, Schafer FP. (Ed.) Springer: New York, 1977.
12. Chen L, Hu T-S and Yao Z-J. *Eur. J. Org. Chem*. 2008; 6175–6182.
13. a) Koefod ARS and Mann KR. *Inorg. Chem*. 1989; **28**: 2285–2290. b) Tasch BS, Brandstatter C, Meghdadi F, Leising G, Froyer G and Athouel L. *Adv. Mater.* 1997; **9**: 33–36.
14. Siegrist CAE, Hefti H, Mayer HR and Schmidt E. *Rev. Prog. Coloration* 1987; **17**: 39–55.
15. a) Yee DJ, Balsanek V and Sames D. *J. Am. Chem. Soc*. 2004; **126**: 2282–2283. b) Sivakumar K, Xie F, Cash BM, Lung S, Barnhill HN and Wang Q. *Org. Lett*. 2004; **6**: 4603–4606.
16. Elangovan A, Lin J-H, Yang S-W, Hsu H-Y and Ho T-I. *J. Org. Chem*. 2004; **69**: 8086–8092.
17. Schiedel M-S, Briehn CA and Bäuerle P. *Angew. Chem. Int. Ed*. 2001; **40**: 4677–4680. *Angew. Chem*. 2001; **113**: 4813–4816.
18. a) Lin W, Long L, Feng J, Wang B and Guo C. *Eur. J. Org. Chem*. 2007; 4301–4304. b) Hania PK, Heijs DJ, Bowden T, Pugžlys AA, Van Esch JH, Knoester J and Duppen K. *J. Phys. Chem.* B 2004; **108**: 71–81.
19. Tasior M, Gryko DT, Pielacińska D, Zanelli A and Flamigni L. *Chem. Asian J*. 2010; **5**: 130–140.
20. Pedersen DS and Rosenbohm C. *Synthesis* 2001; 2431–2434.
21. Hurtley WRH. *J. Chem. Soc.* 1929; 1870–1873.
22. Laha JK, Dhanalekshmi S, Taniguchi M, Ambroise A and Lindsey JS. *Org. Proc. Res. Dev.* 2003; **7**: 799–812.
23. Corrie JET, Munasinghe VRN and Rettig W. *J. Het. Chem.* 2000; **37**: 1447–1456.
24. Specht DP, Martic PA and Farid S. *Tetrahedron* 1982; **38**: 1203–1211.
25. Tkach II, Andronova NA, Savvina LP and Luk'yanets EA. *Chem. Heterocycl. Compd.* 1991; **27**: 259–262.
26. Gryko DT, Wyrostek D, Nowak-Król A, Abramczyk K and Rogacki M. *Synthesis* 2008; 4028–4032.
27. Gryko DT and Koszarna B. *Synthesis* 2004; 2205–2209.
28. Hannick SM and Kishi Y. *J. Org. Chem.* 1983; **48**: 3833–3835.
29. Shirikawa E, Kitabata T, Otsuka H and Tsuchimoto T. *Tetrahedron* 2005; **61**: 9878–9885.
30. Högberg T, Vora M, Drake SD, Mitscher LA and Chu DTW. *Acta Chem. Scand. B* 1984; **38**: 359–366.
31. Poronik EM, Shandura MP and Kovtun YP. *Chem. Heterocycl. Compd.* 2006; **42**: 410–411.