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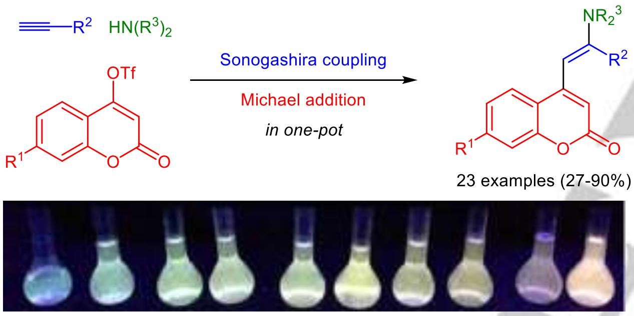
Three-Component Synthesis and Photophysical Properties of Novel Coumarin-based Merocyanines

Julian Papadopoulos,[a] Kay Merkens,[a] and Thomas J. J. Müller*,[a]

Abstract: Novel *E*-configurated coumarin-based merocyanines were efficiently synthesized by a one-pot three-component Sonogashira coupling-Michael addition starting from triflyl coumarins, terminal alkynes and secondary amines. The photophysical properties of the synthesized yellow to orange merocyanines were studied by UV/Vis and fluorescence spectroscopy and rationalized by Hammett-Taft correlations and DFT and TD DFT calculations. Most compounds were only weakly fluorescent in solution; however, two compounds were investigated in more detail with respect to their aggregation behavior. The system for R^2 = H and NR_2^3 = pyrrolidinyl shows aggregation induced emission at a water content of 40-60% in methanol, while the chromophore with R^2 = p-$Me_2NC_6H_4$ and NR_2^3 = morpholinyl displays considerable aggregation induced emission enhancement with a concomitant red shift at increasing water contents in THF.

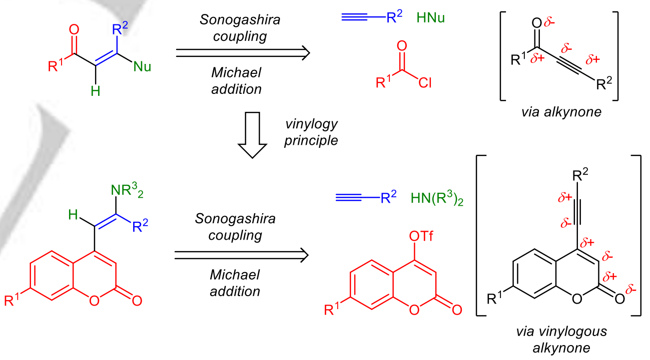


Aggregation induced emission enhancement with red shift

Introduction

Rapid syntheses of novel functional organic materials, such as chromophores, fluorophores and electrophores,[1] with heterocyclic scaffolds became readily accessible in recent years by virtue of the concepts of multicomponent processes[2] and domino reactions.[3] Particularly interesting heterocyclic building blocks for functional π-systems are coumarins (1-benzopyran-2-ones),[4] due to their stable embedded unsaturated lactone structure. In addition, coumarins, finding application as laser dyes,[5] efficient absorbers in dye sensitized solar cells (DSSCs),[6] and emitters in organic light-emitting diodes (OLEDs),[7] are also found to be biologically active as anticancer,[8] anti-inflammatory[9] or antidepressant[10] agents. Among various classes of highly polarizable π-electron systems merocyanines,[11] which can be regarded as neutral push-pull substituted polyenes, have received considerable interest in research and have for instance found application as chromophores with high extinction coefficients in optoelectronics,[12] organic semiconductors,[13] and photovoltaics.[14] As polymethine dyes merocyanines are classically synthesized by conventional aldol or Knoevenagel condensations.[11,15]

As part of our program to devise diversity-oriented syntheses of functional chromophores,[1] we disclosed an efficient consecutive three-component strategy consisting of Sonogashira coupling of acid chlorides and alkynes followed by subsequent cyclocondensation[16] or Michael addition[17] in a one-pot fashion. We reasoned that vinylogous carboxytriflates embedded into a coumarin framework should represent a favorable acceptor moiety for rapidly assembling merocyanines with extended π-conjugation based upon the coupling-addition concept. In addition, the coupling-addition concept would be extended in the sense of the vinylogy principle,[18] where the electrophilicic site of the alkynone's β-position is further transposed to the δ-position in a vinyloguous enynoyl fragment (Scheme 1).



Scheme 1. Retrosynthetic concept of coumarin-based merocyanines by expansion of the Sonogashira coupling-Michael addition concept from alkynone intermediates to vinylogous alkynones.

Here we report a novel microwave assisted synthetic access to coumarin-based push-pull chromophores by a consecutive three-component reaction. In addition, the photophysical properties, aggregation studies in water containing solvent mixtures and structure-property relationships are presented and additionally rationalized by DFT and TD-DFT calculations.

Results and Discussion

Synthesis and Structure

Coumaryl fragments are most favorably employed as coumaryl triflates, which have been shown to be versatile electrophiles for nucleophilic substitution at the β-position of the Michael system

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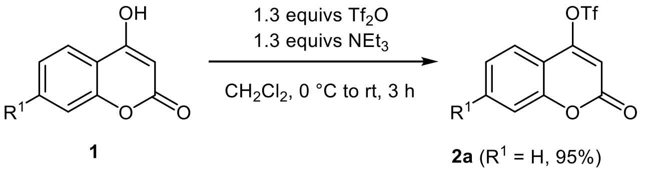
according to addition-elimination mechanisms[19] and favorable substrates for oxidative additions in Suzuki[20] and Sonogashira couplings.[21] Starting from 4-hydroxycoumarin derivatives **1** and triflic anhydride in the presence of triethylamine the coumaryl triflates **2** are easily synthesized in good to excellent yields (Scheme 2).[22]

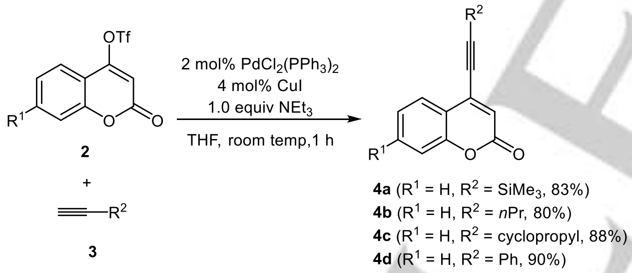


1

2a (R^1 = H, 95%)
2b (R^1 = OMe, 99%)
2c (R^1 = NEt_2, 68%)

Scheme 2. Synthesis of coumaryl triflates **2** by triflation of 4-hydroxycoumarins **1**.

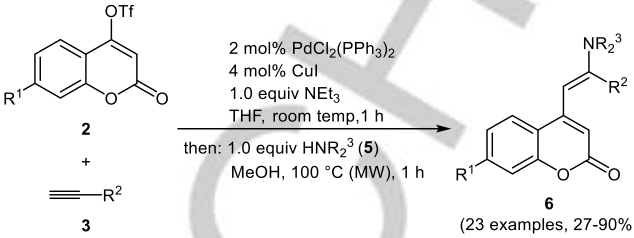
First we set out to probe the alkynylation of the coumaryl triflates **2** with terminal alkynes **3** under modified Sonogashira conditions, i.e. only employing one stoichiometrically necessary equivalent of triethylamine as a base,[23] furnishing 4-alkynyl coumarins **4** in very good yields (80-94%) (Scheme 3). Most favorably, these straightforward alkynylation conditions already proceed smoothly and rapidly at room temperature without optimization, tolerating electron rich coumarins and alkyl, silyl and aryl acetylenes as substrates.



4a (R^1 = H, R^2 = $SiMe_3$, 83%)
4b (R^1 = H, R^2 = *n*Pr, 80%)
4c (R^1 = H, R^2 = cyclopropyl, 88%)
4d (R^1 = H, R^2 = Ph, 90%)
4e (R^1 = OMe, R^2 = Ph, 94%)
4f (R^1 = NEt_2, R^2 = Ph, 88%)

Scheme 3. Synthesis of 4-alkynyl coumarins **4** by modified Sonogashira alkynylation of coumaryl triflates **2** with terminal alkynes **3**.

With these optimal coupling conditions in hand, we set out to develop a concise and straightforward, consecutive one-pot synthesis of coumarin-based merocyanines in a three-component fashion. After alkynylation of coumaryl triflates **2** with terminal alkynes **3** for 1 h the formed 4-alkynyl coumarins **4** (monitored by TLC) were immediately subsequently reacted in the same reaction vessel upon addition of methanolic solutions of various secondary amines **5** under microwave irradiation (100 °C) for 1 h to furnish coumaryl merocyanines **6** as yellow to orange solids in moderate to excellent yields, as exemplified in 23 examples (Scheme 4, Table 1). It is noteworthy to mention that upon applying (TMS)acetylene (**3a**) as a substrate the silyl group is cleaved in the Michael addition step furnishing the aminovinylated derivatives.

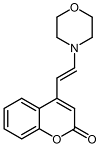
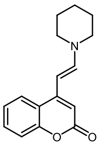


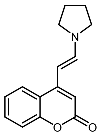
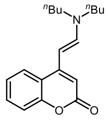
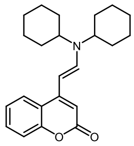
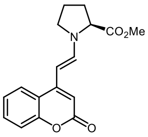
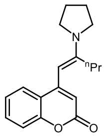
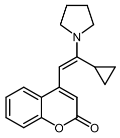
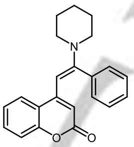
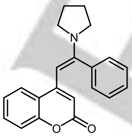
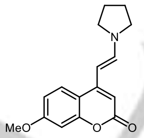
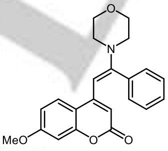
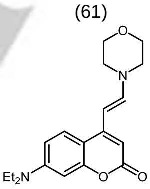
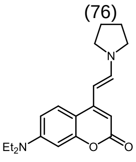
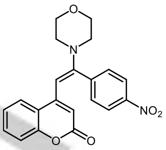
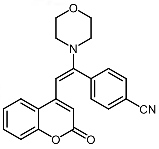
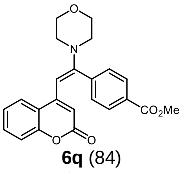
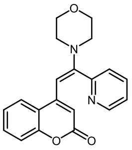
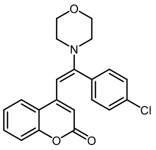
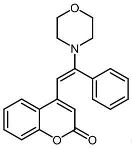
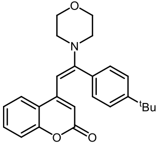
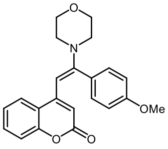
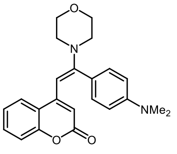
Scheme 4. One-pot coupling-addition synthesis of coumaryl merocyanines **6** in a consecutive three-component fashion.

All new merocyanines **6** were unambiguously characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. Most remarkably all merocyanines **6** are formed stereoselectively, exclusively as *E*-configured isomers, which was corroborated by ^1H NMR spectroscopy by the appearance of the characteristic *trans*-coupling constants (for R^2 = H) or by the appearance of the characteristic cross peaks in the NOESY experiments.

Besides, substituted and unsubstitued coumaryl triflates **2**, aliphatic and (hetero)aromatic terminal alkynes **3** with the full range of electronic substitution, and acyclic and ali(hetero)cyclic secondary amines **5** are well tolerated in this consecutive three-component process, where three points of diversity have been exemplified. Interestingly, also *L*-proline methylester **5f** (Table 1, entry 6) is well accepted, a feature that can be important for in situ labelling of peptides or peptoids. Moreover, the equistoichiometric ratio of coumaryl triflates **2**, terminal alkynes **3**, and secondary amines **5** represent an efficient and also economical process, where the average bond forming efficiency in this three-component process, where three bonds (carbon-carbon bond coupling, amine addition) are being formed, can be calculated to 65-97% per step.

Table 2. One-pot coupling-addition synthesis of coumaryl merocyanines **6** from triflates **2**, alkynes **3**, and amines **5** in a consecutive three-component fashion.[a]

Entry	Coumaryl triflates **2**	Alkynes **3**	Amines HNR_2^3 **5**	Coumaryl merocyanines **6** (yield, %)
1	R^1 = H (**2a**)	R^2 = $SiMe_3$ (**3a**)	morpholine (**5a**)	 **6a** (72)
2	**2a**	**3a**	piperidine (**5b**)	 **6b** (84)

3	**2a**	**3a**	pyrrolidine (**5c**)	 **6c** (79)
4	**2a**	**3a**	di^{n}butyl amine (**5d**)	 **6d** (75)
5	**2a**	**3a**	dicyclohexyl amine (**5e**)	 **6e** (27)
6	**2a**	**3a**	*L*-proline methyl ester hydrochloride (**5f**)	 **6f** (60)
7	**2a**	$R^2 = {}^n$Pr (**3b**)	**5c**	 **6g** (40)
8	**2a**	R^2 = cyclopropyl (**3c**)	**5c**	 **6h** (36)
9	**2a**	R^2 = Ph (**3d**)	**5b**	 **6i** (57)
10	**2a**	**3d**	**5c**	 **6j** (90)
11	R^1 = OMe (**2b**)	**3a**	**5c**	 **6k** (70)
12	**2b**	**3d**	**5a**	 **6l** (61)
13	$R^1 = NEt_2$ (**2c**)	**3a**	**5a**	 **6m** (76)
14	**2c**	**3a**	**5c**	 **6n** (64)
15	**2a**	R^2 = *p*-$O_2NC_6H_4$ (**3e**)	**5a**	 **6o** (84)
16	**2a**	R^2 = *p*-NCC_6H_4 (**3f**)	**5a**	 **6p** (81)
17	**2a**	R^2 = *p*-$MeO_2CC_6H_4$ (**3g**)	**5a**	 **6q** (84)
18	**2a**	$R^2 = C_5H_5N$ (**3h**)	**5a**	 **6r** (86)
19	**2a**	R^2 = *p*-ClC_6H_4 (**3i**)	**5a**	 **6s** (67)
20	**2a**	**3d**	**5a**	 **6t** (47)
21	**2a**	R^2 = *p*-${}^tBuC_6H_4$ (**3j**)	**5a**	 **6u** (72)
22	**2a**	R^2 = *p*-$MeOC_6H_4$ (**3k**)	**5a**	 **6v** (51)
23	**2a**	R^2 = *p*-$Me_2NC_6H_4$ (**3l**)	**5a**	 **6w** (88)

[a] Reaction conditions: 1.00 equiv of coumaryl triflate **2** (1.0 M in THF), 1.10 equiv of terminal alkynes, 0.02 equiv of $PdCl_2(PPh_3)_2$, 0.04 equiv of CuI, and 1.0 equiv of triethylamine; after stirring at rt for 1 h, addition of 1.0 equiv of amine **5** (1 M in methanol), heating in the microwave cavity at 100 °C (hold temp) for 1 h.

Photophysical properties

Most of the obtained title compounds fluoresce weakly but detectable in dichloromethane solution with blue to turquois light upon UV excitation. Therefore, the electronic properties and the electronic structure of all coumaryl merocyanines **6** were investigated in more detail by UV/VIS and static fluorescence spectroscopy (Table 2). The relative fluorescence quantum Φ_f[24] yield of compounds **6n** and **6w** were measured in dichloromethane solution with coumarin 153 as a standard in ethanol (Φ_f = 0.55).[25] As a consequence of the low quantum yields of Φ_f = 0.01 (**6n**) and 0.04 (**6w**), the emission spectra of all other compounds were only recorded qualitatively. In neither case solid state fluorescence could be detected upon eyesight.

Table 2. Selected photophysical properties of merocyanines **6** (recorded in dichloromethane at T = 293 K).[a]

Entry	Compound	Absorption maximum $\lambda_{max,abs}$ [ε] [nm] ($M^{-1}cm^{-1}$)	Emission maximum $\lambda_{max,em}$ [nm]	Stokes shift $\Delta\tilde{\nu}$ [cm^{-1}]
1	**6a**	382 (17500)	456	4200
2	**6b**	395 (17900)	454	3300
3	**6c**	403 (34000)	458	3000
4	**6d**	400 (20500)	453	2900
5	**6e**	406 (28600)	460	2900
6	**6k**	395 (20800)	434	2300
7	**6n**	381 (51600)	446[b]	3800
8	**6o**	331 (12100)	415	6100
9	**6p**	367 (10500)	468	5900
10	**6q**	372 (12100)	460	5100
11	**6s**	372 (9700)	434	3800
12	**6t**	375 (11000)	442	4000
13	**6u**	378 (11800)	426	3000
14	**6v**	382 (12500)	426	2700
15	**6w**	406 (17400)	510[c]	5000

[a] Recorded in CH_2Cl_2 UVASOL (longest wavelength transition). [b] Φ_f = 0.01 (measured in dichloromethane solution with coumarin 153 (Φ_f = 0.55) as a standard in ethanol). [c] Φ_f = 0.04 (measured in dichloromethane solution with coumarin 153 (Φ_f = 0.55) as a standard in ethanol).

All merocyanines **6** possess characteristic intense absorption maxima $\lambda_{max,abs}$ between 372 and 406 nm with molar extinction coefficients ε in a range between 9700 and 51600 $M^{-1}cm^{-1}$. The absorption maximum shifts bathochromically with increasing donor strength from morpholine over piperidine to pyrrolidine. Likewise, the molar extinction coefficient shows a hyperchromic shift from 17900 up to 34000 $M^{-1}cm^{-1}$ (Table 2, entries 1-3). In case of dibutylamino and dicyclohexylamino substitution the extinction coefficient drops significantly, presumably caused by motion of the flexible residue (Table 2, entries 4 and 5) while the emission spectra show no substantial change. In comparison to compound **6c**, increasing the electron density in the coumarin moiety by electron releasing methoxy or diethylamino substituents at position 7 (**6k**, **n**), causes a hypsochromic shift in both absorption and emission spectra. This is presumably affected by superposition of the intensively absorbing subchromophore resulting in an increase of the extinction coefficient up to 51600 $M^{-1}cm^{-1}$ (Table 2, Figure 1).

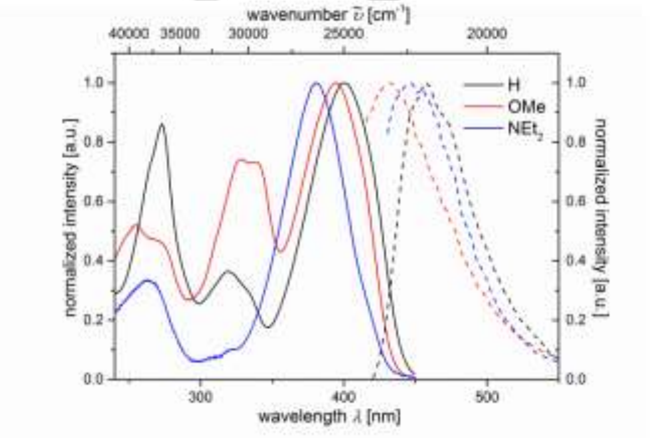


Figure 1. Absorption (solid) and emission (dashed) spectra of merocyanines **6c** (black lines), **6k** (red lines), and **6n** (blue lines) (recorded in CH_2Cl_2 at T = 293 K, λ_{exc} = $\lambda_{max,abs}$).

Furthermore, aggregation studies were performed with merocyanines **6n** and **6w**. Compound **6n** was dissolved in in different methanol/water ratios ranging from 0 to 90% water content (Figure 2). Upon addition of water the relative emission intensity slightly increases in the sense of an aggregation induced emission (AIE)[26] and reaches a plateau between 40 and 60% of water. Above 70% of water the aggregation-caused quenching (ACQ) effect prevails and leads to a decrease of the emission intensity.

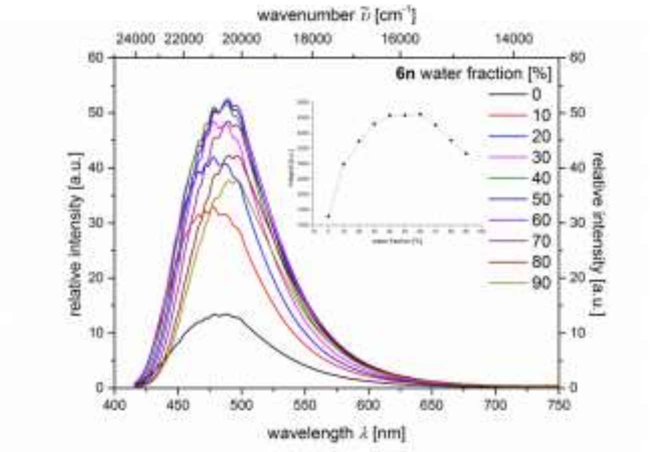


Figure 2. Relative emission spectra of compound **6n** in MeOH/water mixtures containing different water fractions (recorded at T = 293 K, c(**6n**) = 7.43 · 10^{-6} mol/L, λ_{exc} = 392 nm).

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In case of compound **6w** the steady increase of the water fraction in THF/water mixtures results in an aggregation induced emission enhancement (AIEE) with a concomitant bathochromic shift of the emission maximum (Figures 3 and 4), where the emission maximum in THF at $\lambda_{max,em}$ = 518 nm is shifted to 567 nm at a water content 80%. Upon an increase to more than 90% of water the emission intensity rises significantly.

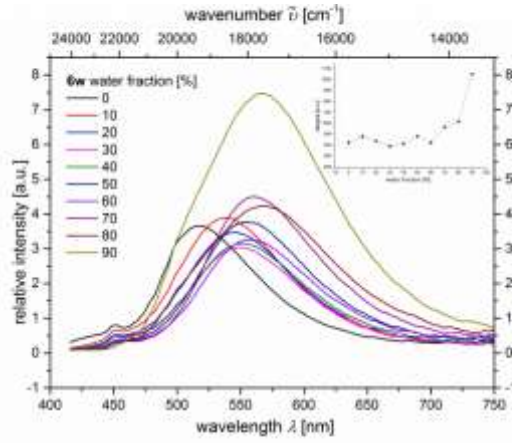

Figure 3. Relative emission spectra of compound **6w** in MeOH/water mixtures containing different water fractions (recorded at T = 293 K, c(**6w**) = 7.43 · 10^{-6} mol/L, λ_{exc} = 392 nm).

Figure 4. Merocyanine **6w** in different THF/water mixtures under UV-light (λ_{exc} = 365 nm, c(**6w**) = 4.89 · 10^{-6} mol/L). From left to right: 0, 10, 20, 30, 40, 50, 60, 70, 80, 90% of water.

In the consanguineous series of the coumaryl merocyanines **6o-q** and **6s-w** bearing a morpholino substituent with a variation of the *p*-phenyl substituent R^2 the electronic absorption and emission behavior are influenced by the remote substituent in the *para*-position of the aryl substituent. The absorption maxima $\lambda_{max,abs}$ appear between 331 and 406 nm and emission maxima $\lambda_{max,em}$ can be detected between 415 and 510 nm. With respect to Dewar's qualitative prediction rules based upon the perturbation theory[27] the alternation of the electron density in the merocyanine moiety can be assumed and a quick prediction of the relative prediction of HOMO-LUMO energy gap can be deduced. The *para*-phenyl substituent with variable electronic character R is located at an unmarked position of the conjugated merocyanine. Therefore, an electron withdrawing group should cause a bathochromic shift, while an electron donating group should shift the absorption maximum hypsochromically (Figure 5).

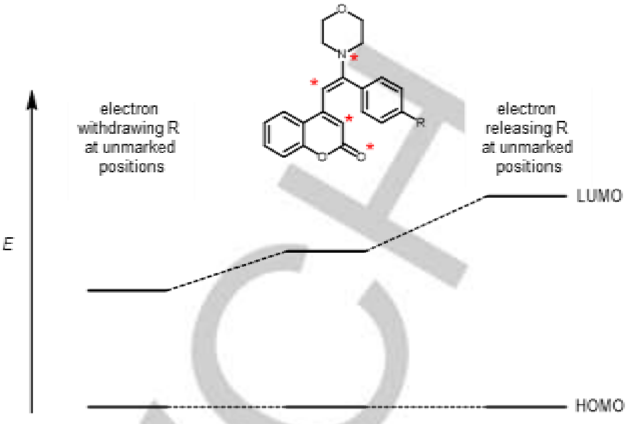

Figure 5. Schematic influence of the substitution pattern on coumaryl merocyanines **6** according to Dewar's qualitative rules based upon perturbation theory**.**

However, Dewar's qualitative prediction does not match with the results of the correlation studies of the longest wavelength absorption maxima $\lambda_{max,abs}$ of the series of compounds **6p**,**q**,**s-v** with the corresponding Hammett-Taft parameters[28] (Figure 6). The linear correlation of $\lambda_{max,abs}$ with σ_p (r^2 = 0.90) with a positive slope resulting in a hypsochromic shift rather accounts for a stabilization of the HOMO by electron withdrawing substituents as supported by DFT calculations (vide infra). In contrast, the emission maxima $\lambda_{max,em}$ give a linear correlation with σ_p (r^2 = 0.83) with a negative slope of −2254, indicating a red shift with increasing acceptor strength. This indicates a polar vibrationally relaxed S_1 state, where the LUMO is lowered by acceptor substitution at unmarked positions. The linear correlation of the Stokes shift $\Delta\tilde{\nu}$ with σ_p (r^2 = 0.92) and a positive reaction parameter of 3227 supports that the change of the electronic structure of the excited state with increasing acceptor strength predominantly governs the emission behavior occurring from a polar vibrationally relaxed S_1 state.

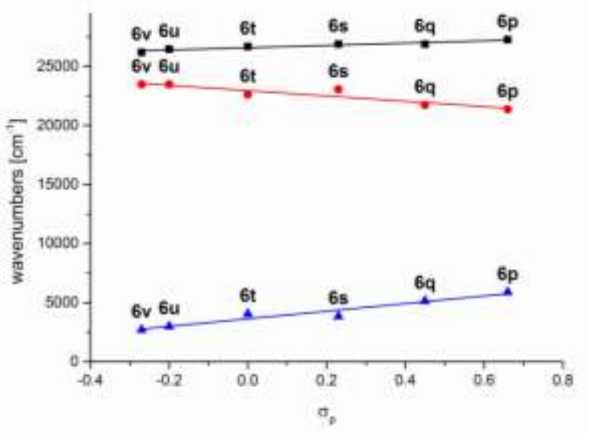

Figure 6. Schematic influence of the substitution pattern on coumaryl merocyanines **6** according to Dewar's qualitative rules based upon perturbation theory**.** Hammett-Taft correlations of the absorption maxima $\lambda_{max,abs}$ (black squares) ($\lambda_{max,abs}$ = 26578 + 973 · σ_p [cm^{-1}], r^2 = 0.90), emission maxima $\lambda_{max,em}$ (red circles) ($\lambda_{max,em}$ = 22947 − 2254 · σ_p [cm^{-1}], r^2 = 0.83 and Stokes shifts $\Delta\tilde{\nu}$ (blue triangles) ($\Delta\tilde{\nu}$ = 3631 + 3227 · σ_p [cm^{-1}], r^2 = 0.92) of the consanguineous series **6p,q,s-w** with σ_p.

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This finding is furthermore supported by the observed positive solvatochromism of compound **6w** determined by Dimroth-Reichardt correlation[29] by plotting the longest wavelength absorption $\lambda_{max,abs}$ (cm^{-1}) against the molar electronic transition energy (kcal mol^{-1}) of the betain dye E_T30 for the corresponding solvent. The emission of the merocyanine **6w** again reveals a positive solvatochromism, where the maximum is shifted from 499 nm in chloroform to 550 nm in methanol (Figure 7). The linear correlation of the Stokes shifts $\Delta\tilde{\nu}$ to the solvent orientation polarizability Δf (Lippert-Mataga plot[30]) gives an excellent fit ($r^2 = 0.95$). By using the Lippert-Mataga equation (1)

$$\tilde{\nu}_a - \tilde{\nu}_e = \frac{2\Delta f}{4\pi\varepsilon_0 hca^3}(\mu_E - \mu_G)^2 + const \qquad (1)$$

the change of dipole moment from ground to excited state can be calculated.

$\Delta\tilde{\nu}_a$ and $\Delta\tilde{\nu}_e$ are the absorption and emission maxima (cm^{-1}), ε_0 is the vacuum permittivity constant ($8.8542 \cdot 10^{-12}$ As $V^{-1}m^{-1}$), h is the Planck's constant ($6.6256 \cdot 10^{-34}$ Js), c is the speed of light ($2.9979 \cdot 10^8$ ms^{-1}) and the orientation polarizability Δf is defined by equation (2):

$$\Delta f = \frac{\varepsilon_r - 1}{2\varepsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (2)$$

with the relative permittivity ε_r and the optical refractive index n of the solvent. The Onsager radius a was calculated from the optimized ground state structure of compound **6w** by DFT calculations. The change in dipole moment from ground to vibrationally relaxed excited state is calculated to $\Delta\mu = 13.4$ D ($4.47 \cdot 10^{-29}$ Cm) using an Onsager radius of 5.66 Å ($5.66 \cdot 10^{-10}$ m). This change in dipole moment accounts for a moderately polar excited state.

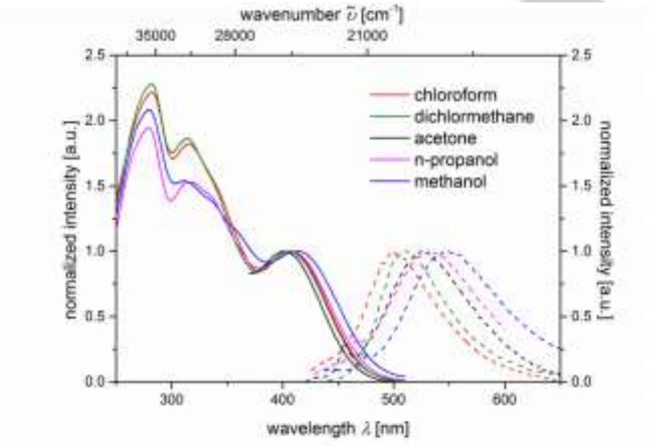

Figure 7. Solvatochromism of compound **6w** (T = 293 K, $\lambda_{exc} = \lambda_{abs,max}$).

Clearly, compound **6w** with the strong donor substituent NMe_2 does not fit in correlation studies within the consanguineous series **6p**,**q**,**s-w**. This deviation can be best rationalized by a change of the dominant chromophore system with the longest wavelength absorption band. This can be further rationalized and illustrated by DFT calculations[31] (B3LYP functional,[32] Pople 6-311++G(d,p) basis set[33]), applying the Polarizable Continuum Model (PCM) with dichloromethane as a solvent,[34] on the selected compounds **6v** (R = MeO) and **6w** (R = NMe_2). The DFT optimized structures as local minima were verified by frequency analyses. The frontier molecular orbitals HOMO and LUMO explicitly show that the coefficient density is delocalized between the morpholinyl and the coumarin moiety for the anisyl substituted system **6v**, the *N*,*N*-dimethylanilino substituent in compound **6w** considerably bears coefficient density in the HOMO. Yet, in both LUMOs, as representative states of the nonrelaxed Franck-Condon absorptions, the coefficient density is predominately localized on the coumarin part of the chromophore with substantial coefficient density at the unmarked β-vinyl morpholino position, thereby rationalizing the red shift of the absorption maximum upon acceptor substitution (Figure 8).

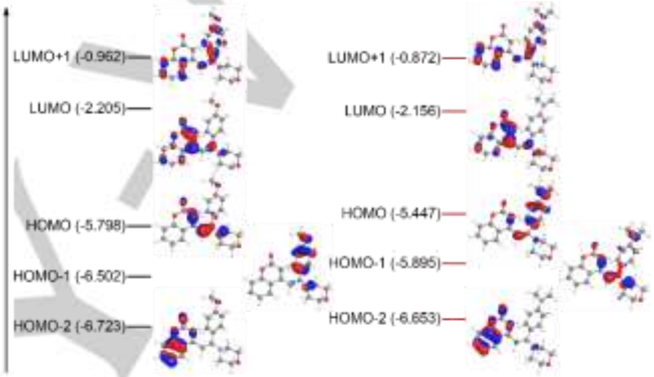

Figure 8. DFT-calculated Kohn-Sham frontier molecular orbitals HOMO, HOMO-1, HOMO-2, LUMO and LUMO+1 of compounds **6v** (left) and **6w** (right) (calculated with B3LYP/6-311++G(d,p) applying the Polarizable Continuum Model (PCM) with dichloromethane as a solvent CH_2Cl_2.

In addition, the TD-DFT calculated optical absorptions of these two donor substituted merocyanines **6v** and **6w** are in good qualitative agreement with the experimentally determined values (Table 3). The longest wavelength absorption maximum of **6v** originates from a dominant HOMO-LUMO transition. Whereas for compound **6w** the two excited states merge in the experimental spectrum, consisting of a dominant HOMO to LUMO and HOMO-1 to LUMO transitions.

Table 3. TD-DFT calculations (B3LYP/6-311++G(d,p)) of the absorption maxima for the merocyanines **6v** and **6w**

Structure	Experimental $\lambda_{max,abs}$ [nm] (most dominant contributions)	Computed $\lambda_{max,abs}$ [nm] (most dominant contributions)	Oscillator strength
6v	382 276	393 HOMO→LUMO (96%) 332 HOMO-1→LUMO (97%) 312 HOMO-2→LUMO (93%) and HOMO→LUMO+1	0.338 0.127 0.166
6w	406 314 282	446 HOMO→LUMO (98%) 371 (HOMO-1→LUMO (97%) 314 HOMO-2→LUMO (88%) and HOMO→LUMO+1 (7%)	0.168 0.333 0.113

Conclusions

In summary we have disclosed a versatile, consecutive three-component synthesis of coumarin-based merocyanines by employing the vinylogous coupling-addition concept in a one-pot fashion. The obtained push-pull chromophores give yellow to orange solutions and weakly blue to turquoise emission is detected by excitation in the longest wavelength absorption bands, depending on the substitution pattern in three points of diversity. The electronic structure can be elucidated by absorption and emission spectroscopy and rationalized by Hammett-Taft correlation studies on consanguineous representatives as well as by DFT and TD DFT calculations. Lippert-Mataga analysis of the *N*,*N*-dimethylanilino substituted merocyanine furnishes a substantial change in dipole moment ($\Delta\mu$ = 13.4 D) upon excitation and relaxation. Two fluorescent chromophores show aggregation induced emission (AIE) in methanol/water and aggregation induced emission enhancement (AIEE) with a concomitant red shift at increasing water contents in THF. The extension of the synthetic concept to more sophisticated AIE and AIEE merocyanines, eventually containing further subchromophores, is currently under way.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.2014xxxxx. Syntheses and analytical characterization of compounds **2**, **4**, and **6**, ^{1}H and ^{13}C NMR spectra of compounds **2**, **4**, and **6**, Hammett correlations, solvatochromism and DFT computed XYZ-coordinates and energies of structures **6v** and **6w**.

Experimental Section

Typical procedure for the one-pot synthesis of merocyanines 6 (compound 6w). In a microwave tube $PdCl_2(PPh_3)_2$ (14.0 mg, 0.02 mmol) and CuI (8.00 mg, 0.04 mmol) were dissolved in THF (1.00 mL) under nitrogen. Triflate **2a** (294 mg, 1.00 equiv) and alkyne **3l** (145 mg, 1.00 equiv) were subsequently added to the reaction mixture. Finally, triethylamine (0.14 mL, 1.00 equiv) was added. The reaction mixture turned from yellow to black and was stirred at room temp for 1 h. Then the amine **5a** (90 mg, 1.00 equiv) and methanol (1.0 mL) was added to the reaction mixture, which was heated in the microwave cavity at 100 °C for 1 h. After cooling to room temp, the solvents were removed and the crude product was purified by flash chromatography on silica gel (n-hexane/ethyl acetate 2:1) to give the desired merocyanine **6w** (331 mg, 88%) as an orange solid, Mp 149 °C; R_f (n-hexane/ethyl acetate 2:1) = 0.11. ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 2.94 (s, 6 H), 3.14 (dd, J = 5.9, 3.4 Hz, 4 H), 3.68 (dd, J = 5.6, 3.9 Hz, 4 H), 5.15 (s, 1 H), 5.62 (s, 1 H), 6.73 (d, J = 8.8 Hz, 2 H), 7.09 (d, J = 8.7 Hz, 2 H), 7.28 (dd, J = 8.2, 1.2 Hz, 1 H), 7.34 (ddd, J = 8.3, 7.2, 1.2 Hz, 1 H), 7.57 (ddd, J = 8.5, 7.4, 1.5 Hz, 1 H), 8.04 (dd, J = 8.0, 1.5 Hz, 1 H). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 39.7 (CH_3), 48.6 (CH_2), 66.0 (CH_2), 92.9 (CH), 106.7 (CH), 112.2 (CH), 116.6 (CH), 119.7 (C_{quat}), 121.1 (C_{quat}), 123.9 (CH), 125.1 (CH), 130.4 (CH), 131.4 (CH), 150.9 (C_{quat}), 151.9 (C_{quat}), 153.1 (C_{quat}), 160.1 (C_{quat}), 160.1 (C_{quat}). EI-MS (70 eV, *m/z* (%)): 377 (26), 376 (100, [M^+]), 375 (38), 348 (18, [$C_{21}H_{20}N_2O_3^+$]), 345 (10), 334 (20), 317 (14), 303 (11), 291 (14), 290 (37, [$C_{19}H_{16}NO_2^+$]), 263 (10), 255 (11), 218 (11), 189 (10), 188 (10), 148 (30), 146 (10), 145 (23), 144 (20), 43 (11). IR: $\tilde{\nu}$ [cm^{-1}] = 2965 (w), 2897 (w), 2857 (w), 2822 (w), 1694 (m), 1678 (m), 1603 (m), 1568 (m), 1518 (m), 1485 (m), 1445 (m), 1396 (m), 1358 (m), 1314 (m), 1304 (w), 1258 (m), 1229 (m), 1188 (m), 1177 (m), 1159 (m), 1113 (s), 1109 (s), 1067 (m), 1026 (s), 930 (s), 905 (m), 837 (m), 820 (s), 800 (m), 785 (s), 754 (s), 750 (m), 735 (m), 719 (m), 700 (m), 685 (w), 652 (m), 645 (m). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [Lcm^{-1}mol^{-1}]) = 282 (7600), 314 (14200), 406 (17400). Emission (CH_2Cl_2): λ_{max} [nm] = 510. Stokes shift $\Delta\tilde{\nu}$ [cm^{-1}] = 5000. Anal. calcd. for $C_{23}H_{24}N_2O_3$ (376.2): C 73.38, H 6.43, N 7.44; Found: C 73.08, H 6.63, N 7.12.

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Keywords: Absorption • additions • correlations • coumarin • DFT calculations • fluorescence • merocyanines • multicomponent reactions • push-pull molecules • Sonogashira coupling

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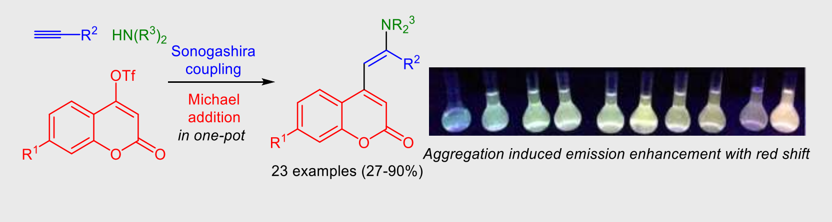

A Sonogashira coupling-Michael addition sequence furnishes coumaryl merocyanines in moderate to excellent yield in a consecutive three-component fashion. Besides tunable electronic properties (UV/Vis and fluorescence spectroscopy, and TD-DFT calculations) selected chromophores display aggregation induced emission (enhancement).

Julian Papadopoulos,[a] Kay Merkens,[a] and Thomas J. J. Müller,[a]*

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Three-Component Synthesis and Photophysical Properties of Novel Coumarin-based Merocyanines