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Rapid Access to Unusual Solid-State Luminescent Merocyanines by a Novel One-Pot Three-Component Synthesis[||]

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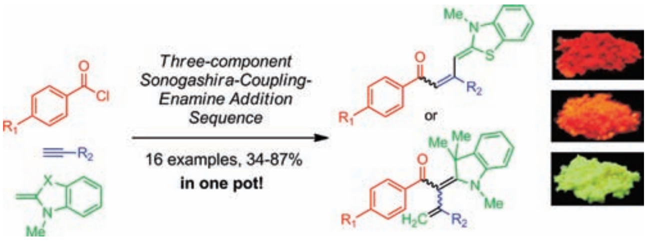
ABSTRACT



A novel consecutive three-component coupling—enamine addition synthesis gives access to three types of diene merocyanines in a selective fashion and in good yields. Moreover, all these push—pull systems are intensely red or yellow emissive in the solid state and display large Stokes shifts.

The quest for novel π-electron systems represents a demanding challenge for organic chemists who cope with the requisition for new functional materials, such as chromophores, fluorophores, and electrophores.[1] Especially the venerable class of merocyanines,[2] i.e. α-donor-ω-acceptor substituted polyenes, has provoked new interest and applications in various areas of science and technology,[3] due to their tunable electronic distribution. In addition merocyanines are also promising chromophores for molecule-based nonlinear optical materials and in photovoltaics.[4] Over the years, general access to these push—pull chromophores always has been Knoevenagel condensations[5] or substitution reactions.[6] However, recently we have established and developed diversity-oriented syntheses of chromophores[7] based upon transition-metal catalysis as an entry to consecutive multicomponent[8] and domino reactions.[9] These productive concepts open excellent

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[||] Dedicated to Prof. Dr. Dr. h. c. mult. Rolf Gleiter on the occasion of his 75th birthday.

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[§] X-ray structure analysis.

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synthetic access to luminescent indolone terminated push–pull dienes, pyrazoles, benzodiazepines, furans, and pyrroles by multicomponent reactions[10,11] and to highly emissive spirocycles in a domino fashion.[9] Furthermore, we devised a straightforward, versatile three-component enaminone synthesis based upon a one-pot coupling–Michael addition sequence.[12] Therefore, we became intrigued in scouting the vinylogous extension with respect to the nucleophile, i.e. the transformation of enamines in the concluding Michael addition step.[13] In addition to scouting the scope of the synthetic methodology we set out to open a new synthetic access to push–pull chromophores with unique luminescence. Here we communicate our findings on the diversity-oriented and highly selective three-component synthesis of a new class of merocyanines in a one-pot fashion. In addition we report the unusual luminescence behavior, which is strongly affected by the substitution pattern.

Commencing with the smooth coupling of benzoyl chlorides **1** and terminal alkynes **2** at room temperature under modified Sonogashira conditions,[12] the anticipated alkynones (the conversion was monitored by TLC) were transformed without isolation by addition of ethanolic solutions of 1,3,3-trimethyl-2-methylene indoline (Fischer's base) (**3**) or 1,2-dimethyl benzothiazolium iodide (**4**) and triethylamine. After heating to 80 °C in a sealed reaction tube for 16 h three different types of diene merocyanines **5**, **6**, and **7** were isolated in moderate to good yields (Scheme 1, Table 1) as crystalline solids with a red (**5**), an orange (**6**) or a bright yellow hue (**7**). The structures of the novel merocyanines were unambiguously assigned by spectroscopic characterization and combustion analysis and later corroborated by X-ray crystal structure analyses for compounds **6b** and **7b** (Figure 1, top and bottom, respectively).[14] Whereas the push–pull butadiene systems **5** and **6** are obtained in a stereoselective fashion, as supported by structural assignments from the crystallography and the occurrence of single sets of signals in all ^{13}C NMR spectra, the vinyl substituted merocyanines **7** are formed as 1:1 mixtures of double bond isomers.

The catalytic generation of the intermediate ynones occurs with expected efficiency.[8,12] In this study only electroneutral and electron-deficient aroyl chlorides have been applied as substrates (1) to enhance the electrophilicity of the ynone in the terminal enamine addition step and (2) to increase the dipole moment of the desired push–pull system. Scouting methodological studies have also revealed that conventional enamines gave unselective product formation arising from solvolysis of the enamines and direct addition of the secondary amino component to the ynone. With respect to chromophore syntheses we therefore continued with 1,3,3-trimethyl-2-methylene indoline (Fischer's base) (**3**)

Scheme 1. Consecutive One-Pot Three-Component Syntheses of Merocyanines **5**, **6**, and **7**

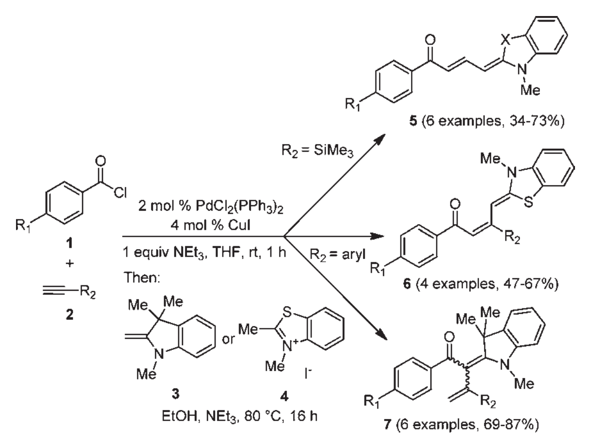

Table 1. Three-Component Syntheses of Merocyanines **5**, **6**, and **7**

entry	benzoyl chloride **1**	alkyne **2**	enamine (precursor)	merocyanines (isolated yield)[a]
1	R_1 = H (**1a**)	R_2 = $SiMe_3$ (**2a**)	**3**	**5a** (34%)[a]
2	**1a**	**2a**	**4**	**5b** (53%)[a]
3	R_1 = CF_3 (**1b**)	**2a**	**3**	**5c** (58%)[a]
4	**1b**	**2a**	**4**	**5d** (73%)[a]
5	R_1 = CN (**1c**)	**2a**	**3**	**5e** (45%)[a]
6	**1c**	**2a**	**4**	**5f** (45%)[a]
7	**1a**	R_2 = p-MeC_6H_4 (**2b**)	**4**	**6a** (48%)
8	**1b**	R_2 = Ph (**2c**)	**4**	**6b** (47%)
9	**1c**	**2b**	**4**	**6c** (53%)
10	**1c**	R_2 = p-$MeOC_6H_4$ (**2d**)	**4**	**6d** (67%)
11	**1a**	**2c**	**3**	**7a** (73%)
12	**1a**	**2b**	**3**	**7b** (76%)
13	**1a**	R_2 = p-ClC_6H_4 (**2e**)	**3**	**7c** (69%)
14	**1a**	R_2 = p-$MeO_2CC_6H_4$ (**2f**)	**3**	**7d** (91%)
15	**1a**	R_2 = p-$O_2NC_6H_4$ (**2g**)	**3**	**7e** (88%)
16	**1c**	**2b**	**3**	**7f** (87%)

[a] The substituent R_2 of all merocyanines **5** (see Scheme 2) is H as a consequence of concomitant desilylation in the addition step.

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(14) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-816762 (**6b**) and -816763 (**7b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

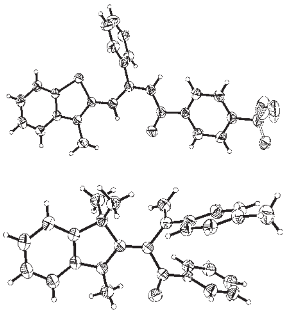


Figure 1. ORTEP plots of compounds **6b** (top) and **7b** (bottom).

or 1,2-dimethyl benzothiazolium iodide (**4**) as an enamine precursor. Most remarkably, a slight electronic difference of the Fischer's base over the **4** derived *S*,*N*-ketene acetal accounts for the selective formation of the unexpected addition products **7**. The connectivity of **7** suggests that formally a (2 + 2)-cycloaddition with subsequent electrocyclic cyclobutene ring opening has occurred. The latter step is also supported by the occurrence of the 1:1 isomeric mixture arising from a conrotatory ring opening in either direction with almost equal preference.

Therefore, the consecutive three-component synthesis of merocyanines **5**, **6**, and **7** can be mechanistically rationalized as follows (Scheme 2). After formation of the ynone **8** by Sonogashira coupling from acid chloride **1** and alkyne **2**, Fischer's base (**3**) or the in situ generated *S*,*N*-ketene acetal **9** (in situ generated from the benzothiazolium salt **4**) most likely attacks the ynone as an enamine nucleophile at the β-position furnishing the zwitterions **10**. The zwitterionic intermediates **10** undergo either prototropy assisted by ethanol to give the push–pull dienes **5** and **6** or 1,4-dipolar cyclization generating the cyclobutene **11**, which upon electrocyclic ring opening furnishes the unexpected merocyanine **7**.

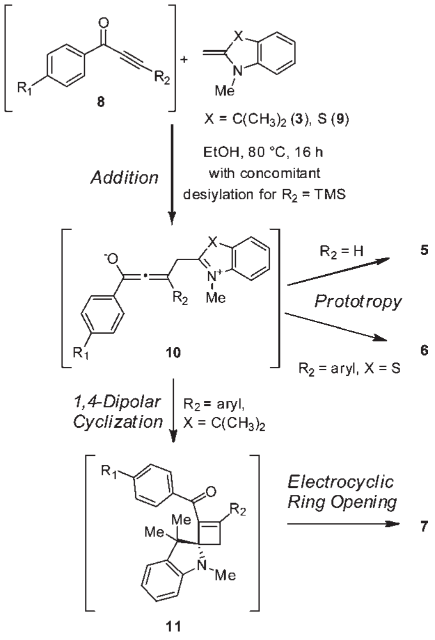
Most interesting are the optical properties of title compounds **5**, **6**, and **7** (Table 2). The absorption maxima of all substances were recorded in dichloromethane at room temperature. Furthermore, thin films of the merocyanines **5a** and **5b**, **6**, and **7** were prepared by slow evaporation from dichloromethane solutions to additionally determine absorption in the amorphous solid state. Compounds **5c**–**f** showed a considerable tendency to crystallize instead of forming films. The comparison of the longest absorption wavelengths of substance class **5** clearly reveals the possibility of fine-tuning the electronic structure by the choice of the starting materials (Table 2, entries 1–6, 450–496 nm).

Table 2. Selected Optical Properties of Merocyanines **5**, **6**, and **7**

		absorption		emission
entry	merocyanine	$\lambda_{max,abs}$ [nm] (ε [L mol/cm]) solution	$\lambda_{max,abs}$ [nm] (film)	$\lambda_{max,em}$[nm] (Φ_f [%])[a] solution
1	**5a**	450 (53 400)	452	512 (3)
2	**5b**	473 (51 800)	482	523 (1)
3	**5c**	464 (47 000)	–	528 (4)
4	**5d**	486 (51 200)	–	544 (3)
5	**5e**	474 (42 400)	–	564 (≤1)
6	**5f**	496 (41 500)	–	574 (≤1)
7	**6a**	492 (53 600)	509	–
8	**6b**	504 (65 800)	522	–
9	**6c**	513 (43 400)	535	–
10	**6d**	516 (28 900)	540	–
11	**7a**	402 (12 700)	401	–
12	**7b**	400 (19 400)	402	–
13	**7c**	401 (12 300)	403	–
14	**7d**	400 (14 100)	400	–
15	**7e**	395 (13 300)	393	–
16	**7f**	417 (16 800)	421	–

[a] Recorded in dichloromethane ($c = 10^{-6}$ M) upon irradiation at $\lambda_{max,abs} \pm 10$ nm with coumarine 6 ($\Phi_f = 78\%$ in ethanol) as a standard.

Scheme 2. Mechanistic Rationale for the Formation of the Merocyanines **5**, **6**, and **7**



Electron-withdrawing substituents R_1 enhance the dipolar character of the π-system **5** causing a bathochromic shift in the absorption spectra. In addition, on the donor part the polarization and polarizability can be increased by switching from a Fischer base to the more electron-rich 3-methyl-2-methylene-2,3-dihydro-benzo-[*d*]-thiazole, again accompanied by a bathochromic shift. A similar trend can be observed for the donor–acceptor dienes **6**, where stronger electron-withdrawing substituents R_1 cause a red shift of the longest absorption wavelength bands (Table 2, entries 7–10, 492–516 nm). Apparently, the substituent R_2 does not affect the absorption maxima (Table 2, entries 8–9). Expectedly, due to the shorter conjugated π-chromophore the merocyanines **7** display shorter absorption wavelengths (Table 2, entries 11–16, 395–417 nm). Again, the electron-withdrawing substituent R_1 shifts the absorption maximum bathochromically (Table 2, entry 16), whereas R_2 exerts only a minor influence (Table 2, entries 11–15). With respect to the oscillator strengths, as reflected by the extinction coefficients, the shorter chromophore **7** expectedly shows smaller values than those for more extended dienes **5** and **6**.

Solution luminescence could only be measured for the merocyanines **5**, whereas the emission of compounds **6** and **7** is essentially quenched in solution (Figure 2).

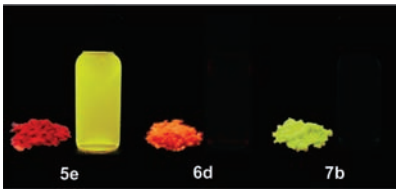


Figure 2. Solid state (left) and solution (in dichloromethane) luminescence of compounds **5e**, **6d**, and **7b** (right) (irradiation at λ_{exc} = 366 nm).

The emission quantum yields Φ_f of compounds **5a**–**f** are found in the low range between 1 and 4%. Nevertheless, these dienes take in a unique position, not only in comparison to all other push–pull systems **6** and **7** but also with respect to indolone terminated push–pull dienes,[11] which are nonluminescent in solution as well. Interestingly, upon transition from solution to the solid state all push–pull chromophores **5**, **6**, and **7** evidently display considerable luminescence (for the naked eye). A closer inspection of the solvent polarity effects on the optical properties reveals positive absorption and emission solvatochromism of merocyanine **5e** (Figure 3). Linear correlations of the longest wavelength absorption (r^2 = 0.92) and emission (r^2 = 0.97) maxima can be obtained as well as Stokes shifts (r^2 = 0.99) with solvents of variable polarity by plotting against Reichardt's $E_T(30)$ values.[15]

The correlation of the Stokes shifts to the empirical $E_T(30)$ values show an excellent goodness of fit (r^2 = 0.99), whereas the correlation to Lippert–Mataga polarity parameters[16] of the solvents is relatively poor (r^2 = 0.90), caused by the poor fit of dioxane. The empirical LFER indicates a low dipole moment of the electronic ground state accompanied by a minor charge transfer in the excited Franck–Condon state by an S_0–S_1 transition.[17] However, the vibrationally relaxed S_1 state displays a significantly higher dipole moment due to the enhanced charge-transfer character. As a consequence the effect of the solvent polarity on the emission encompasses a red shift of 860 cm^{-1} upon increasing the solvent polarity from methyl cyclohexane to benzonitrile. As supported by the X-ray structure analysis of compound **6b** the *anti*-parallel alignment and self-organization by π–π-stacking of the merocyanines **5** and **6** enhance the polar microenvironment.

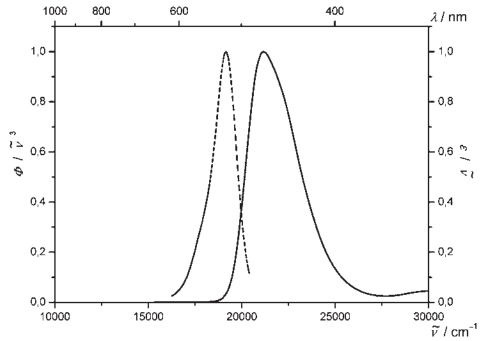


Figure 3. Normalized absorption (—) and emission spectra (---) of compound **5e** (recorded in CH_2Cl_2 at 298 K and at c(**5e**) = 10^{-3} M (absorption) and c(**5e**) = 10^{-6} M (emission)).

In conclusion we have disclosed a novel consecutive three-component coupling–enamine addition sequence selectively giving rise to three types of diene merocyanines with a flexible substitution pattern. The occurrence of vinyl substituted push–pull alkenes **7** accounts for a dipolar addition intermediate, which is sterically and electronically sensitive either toward 1,4-dipolar cyclization with subsequent cyclobutene ring opening giving rise to the formation of the short push–pull systems **7** or toward prototropy furnishing the push–pull dienes **5** and **6**. Most remarkably all merocyanines are red (**5** and **6**) or yellow (**7**) emissive in the solid state. Further studies addressing the three-component methodology and more detailed photophysical and computational investigations to elucidate the electronic structure are currently underway.

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Supporting Information Available. Experimental and analytical details for the three-component synthesis of merocyanines **5**, **6**, and **7**; NMR, absorption and emission spectra of compounds **5**, **6**, and **7**; solvatochromicity data of compound **5e**; crystallographic data; figures; and crystal packing of compounds **6b** and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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