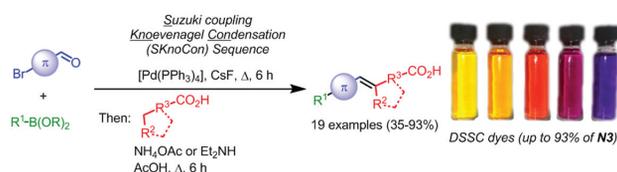


Consecutive Three-Component Synthesis of Donor-Substituted Merocyanines by a One-Pot Suzuki–Knoevenagel Condensation Sequence

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Received: 29.10.2019

Accepted after revision: 17.12.2019

DOI: 10.1055/s-0040-1702148; Art ID: 190021

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Abstract The consecutive three-component Suzuki–Knoevenagel condensation (SuKnoCon) synthesis is an efficient, modular one-pot synthetic approach to donor-substituted merocyanines with carboxylic acid functionality. A library of 19 dyes is readily accessible and their electronic properties can be assessed by cyclic voltammetry and absorption and emission spectroscopy. In addition, for illustration of the utility of this concise one-pot concept, several dyes from this library were identified to be well suited as DSSC dyes with relative efficiencies reaching up to 93% of Grätzel's dye N3.

Key words condensation, catalysts, dyes, merocyanines, multicomponent reactions, solar cells

Introduction

The rational design of small molecules as functional π -electron systems,¹ which are the foundation of modern organic electronics and solar energy conversion, increasingly requires efficient and efficacious ways of synthesis. Many of these functional molecules are chromophores that are employed as active ingredients, for instance, in organic light-emitting diodes,² organic field-effect transistors,³ dye-sensitized solar cells (DSSCs),⁴ and organic photovoltaics (OPVs).⁵ For optimizing the photophysical, electrochemical, and materials' properties of functional chromophores, concise and practical syntheses, eventually in a one-pot fashion, define a challenging goal. Multicomponent reactions (MCRs),⁶ which represent a reactivity-based concept,⁷ can be conducted in domino, sequential, or consecutive mode and promise elegant solutions to this quest. Over the past one and

a half decades, MCRs have consequently been developed in the sense of diversity-oriented syntheses of chromophores, fluorophores, and redox-active molecules.^{8,9} Most fruitfully, the chromogenic approach leads to the formation of the functional chromophore by virtue of the employed MCR.

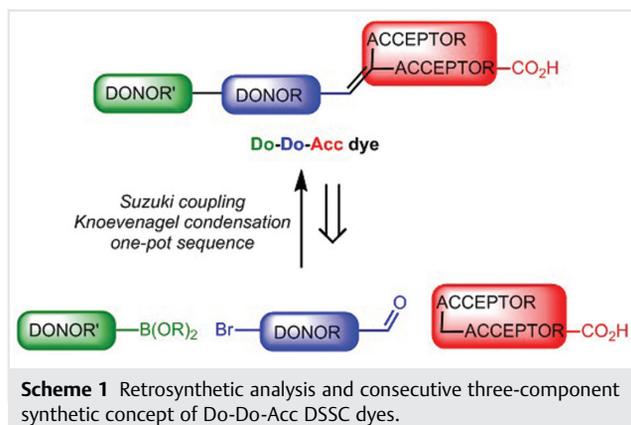
Donor heterocycles,¹⁰ such as phenothiazines and carbazoles, are particularly interesting due to their pronounced reversible oxidation potentials, electro- and photochromicity,¹¹ and luminescence,¹² electronic features that qualify (oligo)phenothiazines as donors in donor-acceptor conjugates with photoinduced electron transfer characteristics,¹³ as hole transport materials,¹⁴ and for applications in mesoporous organosilica hybrid materials.¹⁵

From various de novo syntheses of luminescent heterocycles and push-pull systems^{8,9} and studies on excited-state properties of phenothiazinyl-based merocyanines^{12a} and their DSSC characteristics,¹⁶ we reasoned that a general one-pot synthesis of merocyanine-type donor-donor-acceptor (Do-Do-Acc) dyes for DSSCs can be envisioned in the sense of a three-component Suzuki–Knoevenagel condensation (SuKnoCon) sequence. To our surprise, the concatenation of Suzuki arylation and Knoevenagel condensation in a one-pot process for the synthesis of functional dyes, which would be extremely useful, has not been reported to date. According to this concept, an auxiliary donor, a donor, and an acceptor with carboxylic acid functionality for ligation to TiO₂ should be assembled to the functional DSSC chromophore in a consecutive MCR fashion (Scheme 1).

Here, we communicate our first findings on this straightforward synthetic approach, its variability by virtue of three points of diversity, and representative electronic properties (absorption, emission, oxidation potential, and DSSC behavior) of the obtained chromophore library.

Results and Discussion

Recently we could show that merocyanines containing 7-substituted 10*H*-phenothiazin-3-yl moieties as a donor fragment are readily synthesized from the corresponding carbaldehyde by aldol condensation under mild reaction



conditions.^{12a,16c} In turn the 7-substituted phenothiazine carbaldehydes were accessed from 7-bromo derivatives as ultimate precursors. Inspired by Suzuki–aldol cascade processes,¹⁷ we therefore reasoned that the mildly basic reaction conditions of Suzuki arylations might be excellently suited for introducing electron-rich conjugated substituents and condensations with methylene-active acceptor moieties might be efficiently conducted in a consecutive one-pot process.

Based on our previous experience in the Suzuki coupling of bromoaldehydes and Knoevenagel condensations of the resulting aldehydes in a stepwise fashion,^{12a,16c} we preselected suitable Pd catalysts and bases for the Suzuki reaction as well as piperidine or ammonium acetate as an organocatalyst in the terminal Knoevenagel condensation for concatenating the steps to a consecutive three-component process. As a model reaction, the formation of dye **4a** from *p*-tolyl boronic acid (**1a**), 4-bromobenzaldehyde (**2a**) as a structurally simple bifunctional electrophile, and *N*-methyl rhodamine (**3a**) were employed for establishing the SuKnoCon sequence (Scheme 2, Table 1). The conversion was monitored by TLC and the isolated yields obtained under identical workup conditions were considered as a semiquantitative measure in this optimization study.

Although several other Pd catalysts were prescreened, it turned out that Pd(PPh₃)₄ in combination with Cs₂CO₃ or CsF as bases in the Suzuki reaction not only gave consistently high yields in the sequence but also allowed for omitting water as a cosolvent in the Suzuki reaction (Table 1, entries 3 and 6). Ammonium acetate proved to be superior over piperidine (acetate), a classical Knoevenagel

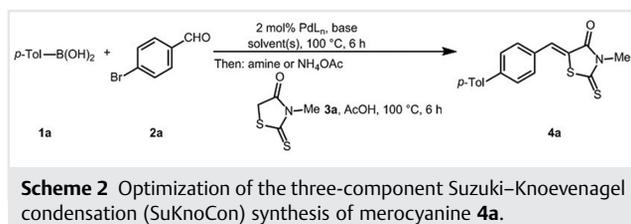


Table 1 Optimization of the one-pot synthesis of merocyanine **4a**

Entry	Pd catalyst	Base	Solvent	Amine catalyst	Merocyanine 4a ^a
1	Pd(OAc) ₂ /PPh ₃	K ₂ CO ₃	H ₂ O/DME	NH ₄ OAc	81% ^b
2	Pd(PPh ₃) ₄	K ₂ CO ₃	H ₂ O/DME	NH ₄ OAc	88% ^c
3	Pd(PPh ₃) ₄	Cs ₂ CO ₃	1,4-Dioxane	NH ₄ OAc	85% ^d
4	Pd(PPh ₃) ₄	K ₂ CO ₃	1,4-Dioxane	Piperidine	68%
5	Pd(PPh ₃) ₄	CsOAc	1,4-Dioxane	–	79% ^e
6	Pd(PPh ₃) ₄	CsF	1,4-Dioxane	NH ₄ OAc	94% ^c

^aYield after chromatography on silica gel.

^bThe Suzuki reaction proceeds with 92%, if the coupling product is isolated.

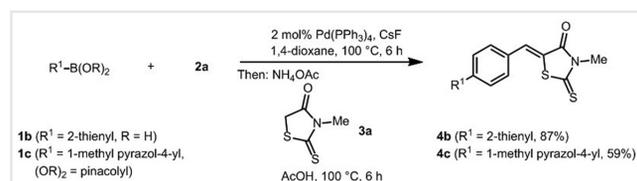
^cThe Suzuki reaction proceeds with 98%, if the coupling product is isolated.

^dThe Suzuki reaction proceeds with 89%, if the coupling product is isolated.

^eThe Suzuki reaction proceeds with 94%, if the coupling product is isolated.

condensation organocatalyst (Table 1, entries 1–3 and 6). Interestingly, CsOAc dispenses from using an additional catalyst in the condensation step, however, furnishing dye **4a** in a slightly lower yield (Table 1, entry 5). Upon transposing the conditions of entry 6 to 3-thienylboronic acid (**1b**) or pinacolyl 1-methylpyrazol-4-yl boronate (**1c**), it immediately came out that the rate of the Suzuki coupling was clearly affected by the nature of the boronic acid derivative. If isolated, the corresponding Suzuki coupling products were obtained in 95 and 65%, respectively. In the consecutive SuKnoCon sequence, the corresponding dyes **4b** and **4c** were obtained in isolated yields of 87 and 59%, respectively, indicating an essentially quantitative Knoevenagel step (Scheme 3).

With these conditions for the one-pot SuKnoCon sequence in hand, we set out to synthesize several Do-Do-Acc dyes **6** containing carboxylic acid functionalities in the acceptor part via variation of the boronic acid derivatives **1**, the bromoaldehyde **2**, and the methylene active acids **5** (Scheme 4).¹⁸ In addition, we also considered 7-bromo carbazole carbaldehyde as a building block, since carbazole donors also have been identified to be relevant donor constituents in DSSCs.¹⁹ The obtained dyes **6** were quite stable in the solid state and in deaerated solutions, as qualitatively assessed by leaving stoppered test tube solutions under indirect daylight in the lab for several months. This accounts for a considerable stability against air oxidation, which was a problem in the first series of phenothiazine-based dyes with pyrrolidene substituents.^{16c}



Scheme 3 Variation of boronates: SuKnoCon synthesis of the dyes **4b** and **4c**.

Table 2 Selected electronic properties (cyclic voltammetry, absorption, and emission) and DSSC characteristics of selected dyes **6–8**

Entry	Dye	Cyclic voltammetry		Absorption	Emission	Excited state reduction potential		DSSC characteristics ^a					
		$E_0^{0/+1bc}$	$E_0^{+1/+2bc}$	$\lambda_{\max,abs}(\epsilon)^d$	$\lambda_{\max,em}^e$	E_{0-0}^f	$E(S^+/S^*)$ vs. NHE ^g	IPCE	j_{sc}	U_{oc}	FF	$x\eta$ (dye)	η (dye)/ η (8)
		[V]	[V]	[nm] ($[M^{-1} cm^{-1}]$)	[nm]	[eV]	[V]	[%]	[mA cm ⁻²]	[mV]		[%]	[%]
1	7 ^[16c]	0.69	0.87	503 (18,000)	688	2.03	-1.15	24	4.46	683	0.60	1.9	45
2	6b	0.65	0.91	498 (22,000)	643	2.16	-1.31	25	4.51	736	0.61	2.0	48
3	6c	0.86	1.12	487 (28,000)	646	2.17	-1.11	16	2.95	633	0.58	1.1	26
4	6d	1.26	- ^h	457 (37,000)	540	2.50	-1.04	13	1.74	574	0.48	0.5	12
5	6g	0.65	1.20	546 (20,000)	- ⁱ	- ⁱ	- ⁱ	5	1.26	637	0.56	0.5	12
6	6i	0.90	1.54	452 (12,000)	618	2.27	-1.17	89	7.19	777	0.55	3.1	74
7	6j	0.65	0.96	467 (15,000)	620	2.26	-1.41	93	6.93	785	0.56	3.9	93
8	6l	0.68	1.27	498 (20,000)	588	2.22	-1.34	45	4.19	738	0.56	1.7	40
9	6m	1.28	- ^h	410 (50,000)	523	2.66	-1.18	83	3.64	712	0.57	1.5	36
10	6n	0.69	1.24	590 (26,000)	- ⁱ	- ⁱ	- ⁱ	12	3.41	645	0.54	1.2	29
11	8 (N3)	- ^j	- ^j	541 (14,000)	- ^j	- ^j	- ^j		11.44	745	0.49	4.2	100

^aRecorded upon irradiation with simulated sun light AM 1.5G (100 mW cm⁻²) at $T = 293$ K, thickness of the TiO₂ film of 13 μ m, irradiation area of 0.78 cm².

^bRecorded in CH₂Cl₂, $T = 293$ K, $v = 100$ mV s⁻¹, electrolyte: [Bu₄N][PF₆], Pt-working electrode, Pt-counter electrode, Ag/AgCl reference electrode.

^c $E_0 = (E_{pa} + E_{pc})/2$ referenced to [Fc]/[Fc]⁺ = 0.45 V²² or [Cp⁺₂Fe]/[Cp⁺₂Fe]⁺ = -0.095 V.²²

^dRecorded in CH₂Cl₂, $T = 293$ K, $c = 10^{-3}$ M.

^eRecorded in CH₂Cl₂, $T = 293$ K, $c = 10^{-6}$ M.

^f E_{0-0} : the energy of the hypothetical 0–0 transition determined from the intersection of the absorption and emission bands.

^gReduction potential of the excited state $E(S^+/S^*) = E_{1/2}^{0/+1} - E_{0-0}$, with $E_{1/2} = E_0 + 0.198$ V.

^hOutside of the measuring range.

ⁱNo detectable fluorescence.

^jNot determined.

estimated from the first ground-state oxidation potentials $E_0^{0/+1}$. A comparison of ground- and excited-state oxidation potentials with the potentials of the conduction band (cb) of TiO₂ [$E^0(\text{cb TiO}_2) = -0.5$ V vs. NHE] and the iodide/triiodide electrolyte [$E^0(I_3^-/I^-) = 0.54$ V vs. NHE]^{16c} reveals that all investigated dyes **6** are well suited as sensitizers for DSSC devices based on a TiO₂ photoanode and an iodide/triiodide electrolyte (Figure 1). Electron transfer from the dyes' excited states into the conduction band of TiO₂ and the

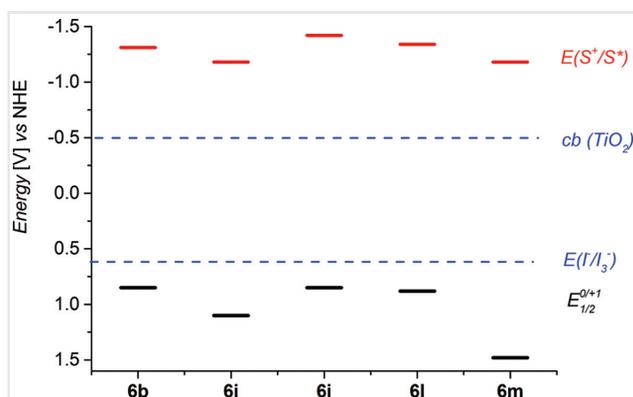


Figure 1 Schematic energy level diagram for selected dyes **6** ($E^0(\text{cb TiO}_2) = -0.5$ V vs. NHE; $E^0(I_3^-/I^-) = 0.54$ V vs. NHE).

regeneration of the oxidized dyes by the electrolyte were thermodynamically feasible.

A comparison of solar-to-electric conversion efficiencies η (**dye**) on an absolute basis is difficult, since systematic mistakes might occur in the preparation of the DSSC device. To a large extent, this is dependent on the preconditioning of the TiO₂ layer, immersion of the dye solutions, and subsequent treatment. Therefore, we decided, as previously reported for highly efficient indoline dyes,²⁰ to reference our dyes to compound **8 (N3)**²¹ by giving a relative measure η (**dye**)/ η (**8**). Under the conditions of our setup, η (**8**) reproducibly gives a solar-to-electric conversion efficiency of 4.2%. Because the incident photon-to-current conversion efficiencies (IPCEs) of the dyes **6b**, **6i**, **6j**, and **6l** are relatively high and stretch over a broad region in the UV/Vis (IPCE > 20% up to $\lambda = 550$ nm), the measured short-circuit photocurrent densities j_{sc} (Table 2, Figure 2) appear in the order of value of reference **N3**.

Based on these relative solar-to-electric conversion efficiencies, previously reported phenothiazinyl-phenothiazine rhodanyl acetic acid merocyanine **7**^{16c} (Table 2, entry 1) could only slightly be improved by altering the terminal auxiliary donor to a *p*-bis(anisyl)aminophenyl derivative **6b** (Table 2, entry 2). Carbazolyl thiophene as a donor has a significantly higher oxidation potential and therefore the intramolecular reduction of the charge-separated state is hampered, resulting

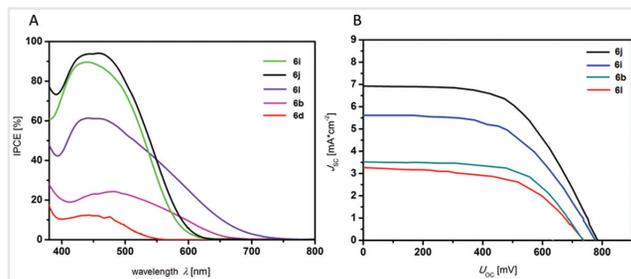


Figure 2 (A) Incident photon-to-current conversion efficiency (IPCE) of DSSCs sensitized by the selected dyes **6** (iodine/triiodide electrolyte). (B) Photocurrent density vs. voltage curves of DSSCs sensitized by the selected dyes **6** (iodine/triiodide electrolyte, under irradiation of AM 1.5 simulated sunlight, 100 mW cm^{-2}).

in a lower relative solar-to-electric conversion efficiency of only 26%. This trend also holds true upon replacing phenothiazine by carbazole as an internal donor for dye **6d**, resulting in a low short circuit voltage U_{OC} (Table 2, entry 4). Expectedly, cyano acrylic acids as acceptor moieties (Table 2, entries 6–9) give inherently higher relative solar-to-electric conversion efficiencies η (**dye**)/ η (**8**) than rhodanyl acetic acid dyes. However, due to the lower oxidation potentials of phenothiazines [$E_0^{O/+1}(\mathbf{6i}) = 0.90 \text{ V}$, Table 2, entry 6] in direct comparison to carbazoles [$E_0^{O/+1}(\mathbf{6m}) = 1.28 \text{ V}$, Table 2, entry 9], although with similar excited-state reduction potentials $E(S^+/S^*)$, similar IPCE values, and similar fill factors (FFs), the higher short-circuit voltages U_{OC} and short-circuit photocurrent densities j_{SC} clearly correlate with the relative solar-to-electric conversion efficiencies [η (**6i**)/ η (**8**) = 74%, (η (**6m**)/ η (**8**) = 36%]. Therefore, phenothiazinyl donors in merocyanines are clearly privileged in their DSSC performance over the more often employed carbazoles,⁴ as clearly supported by this investigated series of merocyanines **6**.

The IPCEs of DSSCs sensitized by the selected phenothiazine dyes **6** (Figure 2A) are in line with the absorption spectra recorded in dichloromethane solution. In the region of the longest-wavelength absorption maxima, the IPCE of **6i** is 89 ($\lambda = 452 \text{ nm}$) and 93% ($\lambda = 467 \text{ nm}$) for **6j**. This mostly transposes to photocurrent density vs. voltage curves of the investigated DSSCs (Figure 2B). Phenothiazinyl internal donor systems **6i** and **6j** give η (**dye**)/ η (**8**) values of 74 and 93% as highest values, almost reaching the value of the reference system **8** (N3) (Table 2, entries 6 and 7). The auxiliary donor R^1 lowers the oxidation potential substantially to $E_0^{O/+1}(\mathbf{6j}) = 0.65 \text{ V}$ (Table 2, entry 7) and enhances the IPCE and the short-circuit voltage U_{OC} and thereby the solar-to-electric conversion efficiency to η (**6j**) = 3.9% [η (**6j**)/ η (**8**) = 93%]. Apparently, the reduction potential of the excited state $E(S^+/S^*)$ as calculated from the lowest oxidation potential, which is centered on the auxiliary donor, is particularly important for generating the charge-separated state. In addition, the *p*-bis(anisyl)aminophenyl

also beneficially matches with the DSSC setup, giving substantially high j_{SC} and U_{OC} values.

Interestingly, the comparison between the chromophores **6b** and **6i**, rhodanyl merocyanine **6b**, and cyano acrylic acid merocyanine **6i** with similar electronic characteristics $E_0^{O/+1}$, $\lambda_{\text{max,abs}}(\epsilon)$, $E(S^+/S^*)$, and even comparable short-circuit voltages U_{OC} clearly underlines the importance of the short-circuit photocurrent density j_{SC} of the DSSC, which is significantly higher for the rhodanyl merocyanine **6b** [$j_{SC}(\mathbf{6b}) = 4.51 \text{ mA cm}^{-2}$] than for the cyano acrylic acid merocyanine **6i** [$j_{SC}(\mathbf{6i}) = 4.19 \text{ mA cm}^{-2}$]. The slightly higher fill factor [FF(**6b**) = 0.61; FF(**6i**) = 0.56] manifests the differences in the relative solar-to-electric conversion efficiencies [η (**6b**)/ η (**8**) = 48%, (η (**6i**)/ η (**8**) = 40%].

An insight into the electronic structure of the relevant absorption bands of dye **6j** in the visible region was obtained via quantum chemical calculations. The geometry of the electronic ground-state structure of dye **6j** (truncated to the *N*-ethyl derivative) was optimized by a density-functional theory (DFT) calculation (B3LYP functional, 6-31G* basis set)²³ and verified by frequency analyses of the local minimum. The electronic absorptions of dye **6j** were calculated on the level of time-dependent DFT (TDDFT) theory employing the B3LYP functional and the 6-31G* basis set.²³ The calculated three longest-wavelength absorption bands appear at 577 (with low oscillator strength), 477, and 365 nm, the latter with a significantly higher oscillator strength (Figure 3), and nicely reproduce the experimental spectrum (see Table 2, entry 7, and Supporting Information, 4.10). Indeed, the calculated band at 577 nm falls into the onset of the broad merocyanine band with a maximum of 467 nm in the experimental spectrum. The lowest energy band with the weakest intensity at 577 nm represents the Franck–Condon S_1 state and can be best characterized by a HOMO–LUMO transition (99%; for details,

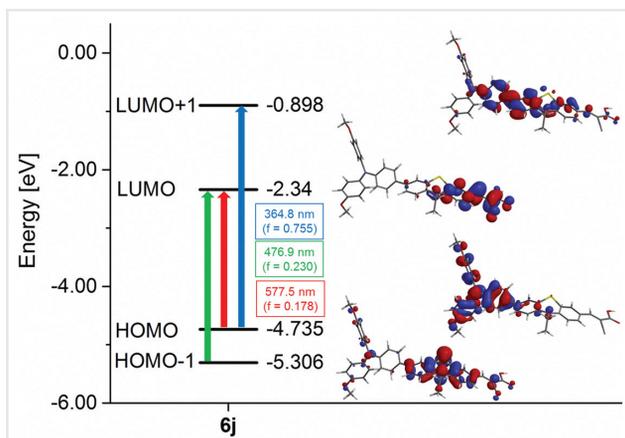


Figure 3 Selected TDDFT-computed (B3LYP 6-31G*) Kohn–Sham FMOs, absorption bands, and oscillator strengths f of dye **6j** (truncated to the *N*-ethyl derivative) representing contributions of the Franck–Condon absorption bands of the first three states S_1 , S_2 , and S_3 .

see the Supporting Information, Table S6). The bands at 477 and 365 nm correspond to S_2 and S_3 states and are represented by HOMO – 1–LUMO ($\lambda_{\max} = 477$ nm) and HOMO–LUMO + 1 ($\lambda_{\max} = 365$ nm) transitions. All the three states consist of considerable charge transfer character, however, with a relatively weak overlap for the HOMO–LUMO transition (S_1) in comparison to the S_2 and S_3 states. Therefore, the initially proposed concept for diversity-oriented syntheses of merocyanine-type Do-Do-Acc for enhancing DSSC characteristics is supported by both experimental and computational results.

Conclusion

Based on the modular synthetic approach to DSSC dyes employing a consecutive three-component SuKnoCon synthesis of the Do-Do-Acc conjugates, efficient DSSC dyes can be rapidly synthesized and their solar cell performance can be semi-quantitatively evaluated. In comparison to Grätzel's dye **N3**, some dyes investigated in this study reached almost a comparable efficiency. In addition, this one-pot concept enables for accessing a huge structural space which can be exploited for establishing reliable structure–property relationships for merocyanines, which can also be considered as suitable absorbers for BHJ (bulk heterojunction) solar cells. Future studies expanding the synthetic concept to more sophisticated dyes and their physical-organic treatment are currently underway.

Funding Information

This study was funded by Evonik Stiftung and Fonds der Chemischen Industrie.

Acknowledgments

The authors cordially thank the Evonik Stiftung (stipend for T.M.) and the Fonds der Chemischen Industrie for financial support.

Supporting Information

Supporting information for this article is available online at: <https://doi.org/10.1055/s-0040-1702148>.

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- (18) **Typical procedure for the consecutive three-component SuKnoCon of merocyanines 6 (compound 6j):** Aryl boronate **1e** (272 mg, 0.64 mmol), bromoaldehyde **2b** (339 mg, 0.53 mmol), cesium fluoride (256 mg, 1.70 mmol), and tetrakis (triphenyl-phosphane)palladium(0) (18 mg, 15 μ mol) were placed in a Schlenk flask with a magnetic stir bar under nitrogen and dry 1,4-dioxane (2.5 mL) was added. The solution was heated to 100 °C under reflux for 16 h. After cooling to room temperature, acetic acid (1.3 mL), the CH-acidic compound **5b** (68 mg, 0.8 mmol), and ammonium acetate (40 mg, 0.5 mmol) were added to the reaction mixture. This mixture was heated under nitrogen to 95 °C under reflux for 8 h. After cooling of the dark red solutions to room temperature, the reaction mixture was diluted with dichloromethane (20 mL) and the organic layer was washed with distilled water until the aqueous phase did not smell like acetic acid. The combined aqueous phases were extracted with dichloromethane and the combined organic layers were dried (anhydrous magnesium sulfate) and the solvents were removed in vacuo. The residue was adsorbed on silica gel (3.2 g) and purified by flash chromatography on silica gel (dichloromethane - dichloromethane/methanol, 20:1). After subsequent drying under vacuo compound **6j** (397 mg, 81%) was obtained as an amorphous dark red solid, Mp 112–119 °C. R_f (dichloromethane/methanol, 10:1) = 0.40. $^1\text{H NMR}$ (300 MHz, acetone- d_6 /CS $_2$ 4:1 + 1 drop of TFA): δ 0.87 (t, 3J = 6.6 Hz, 3H), 0.88 (t, 3J = 6.6 Hz, 3H), 1.19–1.51 (m, 40H), 2.02–2.05 (m, 1H), 3.78 (s, 6H), 3.96 (d, 3J = 7.1 Hz, 2H), 6.86–6.93 (m, 6H), 7.01–7.09 (m, 4H), 7.10 (d, 3J = 8.6 Hz, 1H), 7.16 (d, 3J = 8.7 Hz, 1H), 7.37 (d, 4J = 2.1 Hz, 1H), 7.41–7.47 (m, 3H), 7.89 (d, 4J = 2.1 Hz, 1H), 7.97 (dd, 3J = 8.7 Hz, 4J = 2.2 Hz, 1H), 8.14 (s, 1H). $^{13}\text{C NMR}$ (75 MHz, acetone- d_6 /CS $_2$ 4:1 + 1 drop of TFA): δ 14.5 (CH $_3$), 23.5 (CH $_2$), 26.9 (CH $_2$), 30.20 (CH $_2$), 30.23 (CH $_2$), 30.3 (CH $_2$), 30.42 (CH $_2$), 30.44 (CH $_2$), 30.46 (CH $_2$), 30.49 (CH $_2$), 30.53 (CH $_2$), 30.7 (CH $_2$), 32.0 (CH $_2$), 32.7 (CH $_2$), 35.6 (CH), 52.3 (CH $_2$), 55.7 (CH $_3$), 100.1 (C $_{\text{quat}}$), 115.6 (CH), 116.95 (CH), 117.00 (C $_{\text{quat}}$), 118.18 (CH), 121.0 (CH), 125.6 (C $_{\text{quat}}$), 125.7 (CH), 126.20 (C $_{\text{quat}}$), 126.22 (CH), 126.8 (C $_{\text{quat}}$), 127.6 (CH), 127.7 (CH), 130.6 (CH), 131.8 (C $_{\text{quat}}$), 132.5 (CH), 137.3 (C $_{\text{quat}}$), 141.4 (C $_{\text{quat}}$), 143.0 (C $_{\text{quat}}$), 149.1 (C $_{\text{quat}}$), 151.2 (C $_{\text{quat}}$), 153.7 (CH), 157.2 (C $_{\text{quat}}$), 164.0 (C $_{\text{quat}}$). MS (MALDI-TOF) calcd. for [C $_{60}$ H $_{75}$ N $_3$ O $_4$ S] $^+$: 933.55; Found: 933.6. ESI-HRMS calcd. for [C $_{60}$ H $_{75}$ N $_3$ O $_4$ S] $^+$: 933.5473; Found: 933.5472..
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