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Consecutive Multicomponent Coupling-Addition Synthesis and Chromophore Characteristics of Cyclohexene-Embedded Merocyanines and Cyanines

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Abstract: Merocyanines with embedded butadiene structure in a cyclohexane scaffold are readily obtained by consecutive three-component alkynylation-addition sequences in moderate to excellent yield. Moreover, employing pyrrolidine as an amine provides a pseudo four-component synthesis of related cyanines by carbonyl condensation of the heterocyclic amine in excellent yield. While the merocyanines are essentially nonluminescent, pentamethine cyanines show luminescence with low quantum yield. TDDFT calculations using various exchange correlation hybrid functionals in the gas phase and explicit continuum of dichloromethane underline that the lowest energy absorption bands are highly solvent dependent for a merocyanine and cyanine model. The blue-shifted deviation from the experimental spectra agrees with related merocyanine and cyanine systems. The lowest energy absorption band of merocyanines contains n-π* character, which rationalizes the absence of luminescence.

Keywords: cross-coupling; cyanines; DFT calculations; merocyanines; multicomponent reactions

1. Introduction

Merocyanines [1–6] are structurally characterized as neutral polymethines possessing high extinction coefficients and as highly polarizable π-electron systems. This sets the stage for applications in optoelectronics [7–10], organic semiconductors [11], and photovoltaics [12]. Due to their polar nature and polarizability, their self-assembly in solution enables access to nanoscale objects and supramolecular materials [13,14]. Classical synthetic approaches to merocyanines and many polymethine dyes are conventional aldol or Knoevenagel condensations [1,15–17]. More modern concepts for the synthesis of functional chromophores, such as fluorophores and electrophores [18–20] with heterocyclic scaffolds rely on multicomponent reactions (MCR) [21–24] and domino processes [25,26]. In particular, generating alkynoyl intermediates as part of the catalytic entry to MCR [27] paved the way to several fluorophores in a modular one-pot fashion [28]. In recent years, we have reported concise consecutive three-component syntheses of luminescent merocyanine luminophores based upon the alkynylation-addition sequence [29,30]. Upon derivatization, the merocyanines could also be embedded as covalently bound constituents in highly fluorescent PMMA copolymers [31]. Encouraged by the three-component synthesis of coumarin based luminophores and the tunability of their electronic properties already at the stage of the alkylnyl coumarin intermediates [32], we reasoned that the interesting electronic properties of cyclohexanone-based merocyanines as previously shown by Laschat’s group [33] could be valuable targets for an MCR approach based upon our alkynylation-addition strategy. Here, we report the concise consecutive three-component synthesis of cyclohexanone-based merocyanines and the pseudo four-component synthesis of selected cyanines and the investigation of their UV/Vis absorption properties.
2. Results and Discussion

2.1. Synthesis and Structure

Starting from dimedone (1), i.e., 5,5-dimethylcyclohexane-1,3-dione, a suitable (pseudo) halide is generated by reaction with triflic anhydride to give the corresponding triflate 2 in excellent yield according to the literature (Scheme 1) [34,35].

![Scheme 1. Synthesis of triflate 2.](image)

Based upon our experience with alkynylation of coumarin triflates [32] and their use in consecutive three-component alkynylation-addition sequences [30], we first set out to probe the same reaction conditions in a model reaction of triflate 2, (trimethylsilyl)acetylene (3a), and morpholine (4a). To our surprise a mixture of the merocyanine 5a and the cyanine 6a is formed upon heating to 100 °C in the microwave cavity for 1 h, if triethylamine is employed as a base (Scheme 2, Table 1). While merocyanine 5a can be isolated upon flash chromatography, cyanine 6a is only identified in an inseparable fraction by the mass peaks of the cation and the triflate in the HRMS (Table 1, entries 1–3). However, no product is obtained upon altering the base of the alkynylation step to Hünig’s base (DIPEA) (Table 1, entry 4), while employing potassium carbonate (Table 1, entries 5 and 6) exclusively produces the merocyanine 5a.

![Scheme 2. Multi-component formation of merocyanine 5a and cyanine 6a.](image)

| Entry | Base | Morpholine (4a) [Equivs] | Temperature [°C] | Reaction Time [h] | Merocyanine 5a | Cyanine 6a |
|-------|------|--------------------------|-----------------|-----------------|----------------|------------|
| 1     | NEt₃ | 1                        | 100 (MW)        | 1               | 35%            | +          |
| 2     | NEt₃ | 2                        | 100 (MW)        | 1               | 21%            | +          |
| 3     | NEt₃ | 1                        | rt              | 18              | n.d.           | +          |
| 4     | DIPEA| 1                        | 100 (MW)        | 1               | n.d.           | n.d.       |
| 5     | K₂CO₃ | 1                        | 100 (MW) | 1               | 65%            | n.d.       |
| 6     | K₂CO₃ | 1                        | RT              | 21              | 67%            | n.d.       |

* Yield after chromatography on silica gel, n.d.: not detected on TLC. ** The product is impure after chromatography on silica gel, but identified by HRMS in the fraction, n.d.: not detected on TLC. *** K₂CO₃ (2 equivs) is employed as a base and the reaction time of the alkynylation step is 2 h.

Starting from triflate 2, alkyne 3, and heterocyclic secondary amine 4, potassium carbonate and triethylamine can both be successfully employed in the alkynylation step of
the three-component syntheses of merocyanines 5; however, in most cases the former base gives higher yields after isolation by flash chromatography (Scheme 3).

Scheme 3. Three-component synthesis of merocyanines 5 employing potassium carbonate or triethylamine as a base in the alkynylation step.

Moreover, Fischer’s base (7) can be employed in the addition step of the consecutive merocyanine synthesis using triethylamine as the base in the alkynylation step, albeit, with only a poor overall yield of merocyanine 8 (Scheme 4).

Scheme 4. Three-component synthesis of merocyanine 8.

Intrigued by the formation of cyanine 6a as a byproduct and employing pyrrolidine (4b) as a stronger nucleophile, we set out to probe the selective formation of cyanines 6 in a pseudo four-component fashion. Indeed, upon reaction of triflate 2, alkynes 3 (R₁ = SiMe₃ or Ph), and pyrrolidine (4b) in the presence of triethylamine as a base in the alkynylation step, cyanines 6 is obtained analytically pure and in excellent yield as triflate salts after chromatography on silica gel (Scheme 5). It is noteworthy to mention that piperidine (4c) is obviously not nucleophilic enough to give complete conversion to the corresponding cyanine, which is only identified in the inseparable fraction after flash chromatography.
Scheme 5. Pseudo four-component synthesis of cyanines 6.

The structures of the merocyanines 5 and 8 and the cyanines 6 were unambiguously assigned by NMR spectroscopy and mass spectrometry. The representative discussion of extensive NMR spectroscopy of compound 5e underlines some features of the merocyanines. The geminal methyl groups on the cyclohexenone moiety appear as a singlet at $\delta = 0.79$, indicating the overall planar structure of the merocyanine chromophore in solution (Figure 1). The methylene protons in $\alpha$- and $\gamma$-position to the carbonyl group appear as singlets at $\delta = 2.01$ and 1.65. Methine signals for the $\alpha$- and the $\gamma$-positions of the Michael system are expectedly found a higher field and appear as singlets at $\delta = 5.05$ and 5.41. The methylene protons of the pyrrolidinyl moiety are not well resolved and are found at $\delta = 1.89$ and 3.15.

Figure 1. $^1$H NMR spectrum of compound 5e (CDCl$_3$, 300 MHz, 298 K).

The $E$-configuration of the pyrrolidinyl vinyl substituent can be assigned by the NOESY spectrum, where the pyrrolidinyl $\alpha$-protons at $\delta = 3.15$ and the cyclohexenyl methylene protons at $\delta = 1.65$ give cross-peaks to the merocyanine methine proton at $\delta = 5.05$ (Figure 2).

In addition, the structure of cyanine 6b was corroborated by an X-ray structure analysis (Figure 3) [36], which clearly shows that an $E$-configured isomer was formed in the synthesis. Furthermore, the inspection of the bond lengths of the fully planarized pentamethine part of the chromophore supports the highly delocalized cyanine structure with a small bond length alternation [37] of 0.027 Å for the bonds C1-C6, C6-C5, C5-C7, and C7-C8 (Table 2, ...
entries 2–5), which is typical for nearly symmetrical electron density distribution in cationic cyanine dyes [38].

Figure 2. NOESY spectrum of compound 5e (CDCl$_3$, 600 MHz, 298 K).

Figure 3. Molecular structure of 6b. Displacement ellipsoids are drawn at the 50% probability level; H atoms are drawn with an arbitrary radius.
Table 2. Selected bond lengths of structure 6b.

| Entry | Bond     | Bond Length [Å] |
|-------|----------|-----------------|
| 1     | N1-C1    | 1.316           |
| 2     | C1-C6    | 1.399           |
| 3     | C6-C5    | 1.380           |
| 4     | C5-C7    | 1.404           |
| 5     | C7-C8    | 1.369           |
| 6     | C8-N6    | 1.320           |

2.2. Absorption and Emission Characteristics

Merocyanines 5 and 8 and cyanines 6 that are obtained as yellow to orange solids were investigated by UV/Vis and emission spectroscopy in dichloromethane solution (Table 3). The merocyanines 5 give typically broad, unstructured longest wavelength absorption bands between 365 and 388 nm (Figure 4, Table 3, entries 1–5), also revealing that the maxima redshift with increasing electron donicity of the secondary amine from morpholine over piperidine to pyrrolidine. Extension of the π-system as for merocyanine 8 expectedly causes a redshift of the absorption band to 442 nm (Table 3, entry 6). The absorption solvatochromicity in qualitative UV/Vis measurements is small, similarly as reported for more rigidified merocyanines [33] accounting for a more polyene-like ground state structure of merocyanines 5 and 8. None of the merocyanines, neither 5 nor 8, display any emission upon detection with the naked eye and attempted emission spectroscopy also remains unsuccessful. The cyanines 6b and 6c possess cyanine typical narrow absorption bands at 443 and 459 nm with absorption coefficients exceeding $10^5 \text{ M}^{-1}\text{cm}^{-1}$ (Figure 5, Table 3, entries 7 and 8). Both cyanines are weakly emissive with a sharp emission maximum at 453 nm for cyanine 6b, indicating minimal structural changes in the vibrationally relaxed $S_1$ after photonic excitation, and a broad emission maximum at 513 nm for cyanine 6c. The latter large Stokes shift of 2300 cm$^{-1}$ accounts for more pronounced structural changes upon electronic excitation from the electronic ground state $S_0$ to the vibrationally relaxed $S_1$.

Table 3. Absorption and emission characteristics of selected merocyanines 5 and 8 and cyanines 6 (recorded in CH$_2$Cl$_2$ at $T = 293$ K).

| Entry | Compound | $\lambda_{\text{max,abs}}$ [nm] $^a$ ($\varepsilon$ [M$^{-1}$cm$^{-1}$]) | $\lambda_{\text{max,em}}$ [nm] $^b$ | Stokes Shift $\Delta \tilde{\nu}$ [cm$^{-1}$] $^c$ |
|-------|----------|-------------------------------------------------|----------------|-----------------|
| 1     | 5a       | 373 (71,000)                                    | n.d. $^d$     |                  |
| 2     | 5b       | 373 (71,000)                                    | n.d. $^d$     |                  |
Table 3. Cont.

| Entry | Compound | $\lambda_{\text{max,abs}}$ [nm] $^a$ ($\epsilon$ [M$^{-1}$cm$^{-1}$]) | $\lambda_{\text{max,em}}$ [nm] $^b$ | Stokes Shift $\Delta\nu$ [cm$^{-1}$] $^c$ |
|-------|----------|-------------------------------------------------|-----------------|------------------|
| 3     | ![Compound 3](image1) | 365 (19,000) | n.d. $^d$ | |
| 4     | ![Compound 4](image2) | 383 (22,000) | n.d. $^d$ | |
| 5     | ![Compound 5](image3) | 388 (43,000) | n.d. $^d$ | |
| 6     | ![Compound 6](image4) | 442 (27,000) | n.d. $^d$ | |
| 7     | ![Compound 7](image5) | 443 (114,000) | 459 | 800 |
Table 3. Cont.

| Entry | Compound | $\lambda_{\text{max,abs}}$ [nm] $a$ ($\epsilon$ [M$^{-1}$ cm$^{-1}$]) | $\lambda_{\text{max,em}}$ [nm] $b$ | Stokes Shift $\Delta\tilde{\nu}$ [cm$^{-1}$] $c$ |
|-------|----------|-------------------------------------------------|---------------------------------|---------------------------------|
| 8     | ![Compound 6c](image) | 459 (130,000) | 513 | 2300 |

$^a$ Longest wavelength absorption maximum. $^b$ Emission maximum. $^c$ $\Delta\tilde{\nu} = 1/\lambda_{\text{max,abs}} - 1/\lambda_{\text{max,em}}$ [cm$^{-1}$]. $^d$ Not detected.

Figure 4. Normalized absorption spectra of merocyanines 5c–e (recorded in dichloromethane, c(5) = 10$^{-5}$ M, T = 298 K).

2.3. Calculated Electronic Structure

For assigning the photophysical characteristics of merocyanines 5 and cyanines 6, calculations of the UV/Vis transitions of geometry optimized structures of merocyanine 5b and cyanine 6b were performed on the DFT and TDDFT level of theory using various exchange correlation hybrid functionals (B3LYP [39], PBEh1PBE [40], and CAM-B3LYP [41]) and the 6-311++G** basis set [42], which was chosen to most precisely describe polarization as well as long-range interactions. Besides gas phase calculations, the polarizable contin-
The polarized continuum model (PCM) for the dichloromethane as a dielectric continuum is employed [43] as implemented in the program package Gaussian 16 [44]. The comparative calculations of the first excited states $S_1$ to $S_6$ are summarized in Table 4 (merocyanine 5b) and Table 5 (cyanine 6b). The longest wavelength absorption bands possess high extinction coefficients in the experimental spectra and this aspect is mirrored by high oscillatory strengths in the calculated spectra (see Supplementary Materials).

![Figure 5. Normalized absorption and emission spectra of cyanines 6b and 6c (recorded in dichloromethane, $c(6) = 10^{-5}$ M, $T = 298$ K).](image)

**Table 4.** Experimentally determined longest wavelength absorption band (recorded in dichloromethane at $T = 298$ K) and TDDFT calculated absorption spectra of merocyanine 5b using various functionals and 6-311++G** as a basis set.

| Functional | State | $\lambda_{\text{max},\text{abs exp}}$ [nm] | Oscillatory | Most Dominant | $\Delta E_{\text{calcd-exp}}$ [eV] |
|------------|-------|-----------------|-------------|---------------|-----------------|
|            |       | $\lambda_{\text{max},\text{abs calcd}}$ [nm] | Strength $f$ | Contribution (%) |                           |
| B3LYP *    | $S_1$ | 361.0           | 3.426       | 0.0077        | HOMO-1→LUMO (92%) |
|            |       |                 |             |               | HOMO→LUMO (2%)    |
|            |       |                 |             |               | HOMO→LUMO (97%)   |
|            | $S_2$ | 331.8           | 3.727       | 0.6853        | HOMO-1→LUMO (2%)  |
|            |       |                 |             |               | HOMO→LUMO (97%)   |
|            | $S_3$ | 302.6           | 4.087       | 0.0137        | HOMO→LUMO+1 (97%) |

$\lambda_{\text{max},\text{abs exp}} = 373$ nm/3.327 eV (71,000 M$^1$cm$^{-1}$)
Table 4. Cont.

![Image](image.png)

$\lambda_{\text{max,abs}}$ exp 373 nm/3.327 eV (71,000 M$^{-1}$cm$^{-1}$)

| Functional | State | $\lambda_{\text{max,abs calc}}$ | Oscillatory | Most Dominant | $\Delta E_{\text{calc/exp}}$ |
|------------|-------|-----------------|-------------|--------------|----------------|
|            |       | [nm] | [eV] | Strength $f$ | Contribution (%) | [eV] |
| B3LYP (CH$_2$Cl$_2$) $^b$ | S$_4$ | 272.3 | 4.542 | 0.002 | HOMO→LUMO+2 (91%) | |
|            | S$_5$ | 264.5 | 4.676 | 0.004 | HOMO→LUMO+3 (5%) | |
|            | S$_6$ | 257.9 | 4.796 | 0.0157 | HOMO→LUMO+2 (5%) | |
| B3LYP (CH$_2$Cl$_2$) $^c$ | S$_1$ | 351.5 | 3.523 | 0.0063 | HOMO→LUMO (91%) | 0.596 |
|            | S$_2$ | 315.3 | 3.923 | 0.7332 | HOMO→LUMO+2 (5%) | |
|            | S$_3$ | 230.7 | 5.361 | 0.0137 | HOMO→LUMO (98%) | |
|            | S$_4$ | 222.0 | 5.570 | 0.0063 | HOMO→LUMO+1 (97%) | |
|            | S$_5$ | 211.4 | 5.849 | 0.0049 | HOMO→LUMO+2 (70%) | |
|            | S$_6$ | 211.3 | 5.854 | 0.0093 | HOMO→LUMO+4 (62%) | |
| PBEh1PBE $^a$ | S$_1$ | 351.1 | 3.523 | 0.0063 | HOMO→LUMO (91%) | 0.191 |
|            | S$_2$ | 315.3 | 3.923 | 0.7332 | HOMO→LUMO+2 (5%) | |
|            | S$_3$ | 230.7 | 5.361 | 0.0137 | HOMO→LUMO (98%) | |
|            | S$_4$ | 222.0 | 5.570 | 0.0063 | HOMO→LUMO+1 (97%) | |
|            | S$_5$ | 211.4 | 5.849 | 0.0049 | HOMO→LUMO+2 (70%) | |
|            | S$_6$ | 211.3 | 5.854 | 0.0093 | HOMO→LUMO+4 (62%) | |
| PBEh1PBE (CH$_2$Cl$_2$) $^b$ | S$_1$ | 351.5 | 3.518 | 0.8573 | HOMO→LUMO (99%) | 0.191 |
|            | S$_2$ | 326.3 | 3.791 | 0.0079 | HOMO→LUMO (93%) | |
|            | S$_3$ | 268.0 | 4.616 | 0.0139 | HOMO→LUMO+1 (95%) | |
|            | S$_4$ | 247.4 | 4.998 | 0.0103 | HOMO→LUMO+2 (93%) | |
|            | S$_5$ | 243.3 | 5.084 | 0.0044 | HOMO→LUMO+3 (76%) | |
|            | S$_6$ | 237.7 | 5.204 | 0.0374 | HOMO→LUMO+4 (18%) | |
**Table 4. Cont.**

| Functional | State | $\lambda_{\text{max,abs}}$ | Oscillatory | Most Dominant | $\Delta E_{\text{calcd—exp}}$ |
|------------|-------|-----------------|-------------|---------------|------------------|
| CAM-B3LYP  | S₁    | 318.4 3.884 0.0261 | HOMO→LUMO (78%) HOMO→LUMO+2 (6%) | | |
|            | S₂    | 301.5 4.102 0.6999 | HOMO→LUMO (93%) | | 0.775 |
|            | S₃    | 212.3 5.825 0.0179 | HOMO→LUMO+1 (86%) HOMO→LUMO+6 (7%) | | |
|            | S₄    | 204.2 6.058 0.0063 | HOMO→LUMO+4 (69%) | | |
|            | S₅    | 198.7 6.225 0.1157 | HOMO→LUMO+2 (11%) | | |
|            | S₆    | 197.9 6.250 0.0379 | HOMO→LUMO+4 (6%) HOMO→LUMO+3 (19%) | | |
| CAM-B3LYP (CH₂Cl₂) | S₁    | 343.2 3.604 0.8438 | HOMO→LUMO (98%) | | 0.277 |
|            | S₂    | 298.1 4.149 0.0024 | HOMO→LUMO (80%) HOMO→LUMO+8 (4%) | | |
|            | S₃    | 256.5 4.822 0.016 | HOMO→LUMO+1 (77%) HOMO→LUMO+5 (12%) | | |
|            | S₄    | 234.1 5.282 0.0084 | HOMO→LUMO+3 (77%) HOMO→LUMO+9 (8%) | | |
|            | S₅    | 229.0 5.401 0.0358 | HOMO→LUMO+2 (48%) HOMO→LUMO+4 (21%) | | |
|            | S₆    | 224.9 5.498 0.0206 | HOMO→LUMO+4 (56%) HOMO→LUMO+2 (26%) | | |

* Gas phase calculation in absence of PCM. b Employing PCM for dichloromethane as a dielectric continuum. c Employing a state specific solvation for dichloromethane as a dielectric continuum.

**Table 5.** Experimentally determined longest wavelength absorption band (recorded in dichloromethane at $T = 298$ K) and TDDFT calculated absorption spectra of cyanine $6b$ using various functionals and 6-311+G** as a basis set.

| Functional | State | $\lambda_{\text{max,abs}}$ | Oscillatory | Most Dominant | $\Delta E_{\text{calcd—exp}}$ |
|------------|-------|-----------------|-------------|---------------|------------------|
| B3LYP  a   | S₁    | 362.2 3.415 0.9478 | HOMO→LUMO (100%) | | 0.614 |
|            | S₂    | 250.8 4.931 0.1102 | HOMO→LUMO (76%) HOMO→LUMO+1 (22%) | | |
|            | S₃    | 224.7 5.503 0.0268 | HOMO→LUMO-1 (55%) HOMO→LUMO (28%) | | |
Table 5. Cont.

| Functional | State | \(\lambda_{\text{max,abs calc}}\) [nm] | Oscillatory | Most Dominant | \(\Delta E_{\text{calcd—exp}}\) [eV] |
|------------|-------|-------------------|-------------|---------------|----------------|
|            |       | \([\text{eV}]\) | Strength \(f\) | Contribution (%) |                |
| **S4**     |       | 223.1             | 5.543       | 0.0803        | HOMO→LUMO+1 (45%) HOMO-2→LUMO (34%) |
| **S5**     |       | 219.6             | 5.632       | 0.0075        | HOMO→LUMO+2 (88%) HOMO→LUMO+4 (4%) |
| **S6**     |       | 215.7             | 5.734       | 0.0184        | HOMO→LUMO+4 (77%) HOMO-2→LUMO (12%) |
| **B3LYP (CH\(_2\)Cl\(_2\))** | **S1** | 386.1             | 3.203       | 1.0034        | HOMO→LUMO (100%) |
|            | **S2** | 261.3             | 4.734       | 0.0031        | HOMO→LUMO+1 (95%) |
|            | **S3** | 254.3             | 4.864       | 0.1198        | HOMO→LUMO+1 (95%) |
|            | **S4** | 244.4             | 5.061       | 0.0263        | HOMO→LUMO+3 (63%) |
|            | **S5** | 239.2             | 5.171       | 0.036         | HOMO→LUMO+4 (64%) |
|            | **S6** | 233.7             | 5.292       | 0.1408        | HOMO→LUMO+4 (26%) |
| **B3LYP (CH\(_2\)Cl\(_2\))** | **S1** | 369.0             | 3.357       | 0.8976        | HOMO→LUMO (100%) |
|            | **S2** | 250.2             | 4.944       | 0.0031        | HOMO→LUMO+1 (95%) |
|            | **S3** | 245.6             | 5.036       | 0.1198        | HOMO→LUMO+1 (95%) |
|            | **S4** | 244.2             | 5.065       | 0.0193        | HOMO→LUMO+3 (68%) |
|            | **S5** | 239.2             | 5.170       | 0.0135        | HOMO→LUMO+4 (76%) |
|            | **S6** | 231.8             | 5.335       | 0.0975        | HOMO→LUMO+2 (20%) |
| **PBEh1PBE** | **S1** | 357.5             | 3.460       | 0.9557        | HOMO→LUMO (100%) |
|            | **S2** | 242.7             | 5.096       | 0.1278        | HOMO→LUMO+1 (81%) |
|            | **S3** | 219.4             | 5.638       | 0.0861        | HOMO→LUMO+1 (45%) |
|            | **S4** | 218.0             | 5.673       | 0.0435        | HOMO→LUMO+1 (45%) |
|            | **S5** | 210.5             | 5.875       | 0.0024        | HOMO→LUMO+2 (88%) |
|            | **S6** | 209.6             | 5.902       | 0.0174        | HOMO→LUMO+4 (5%) |
| **PBEh1PBE (CH\(_2\)Cl\(_2\))** | **S1** | 380.4             | 3.252       | 1.0153        | HOMO→LUMO (99%) |
|            | **S2** | 250.2             | 4.944       | 0.0056        | HOMO→LUMO+1 (93%) |
|            | **S3** | 245.6             | 5.036       | 0.1362        | HOMO→LUMO+1 (66%) |
|            | **S4** | 233.5             | 5.297       | 0.0846        | HOMO→LUMO+2 (53%) |
|            | **S5** | 230.7             | 5.360       | 0.0853        | HOMO→LUMO+3 (49%) |

\[\lambda_{\text{max,abs exp}}\ 443 \text{ nm/2.801 eV (114,000 M}\ ^{-1}\ \text{cm}\ ^{-1})\]
Table 5. Cont.

| Functional          | State | $\lambda_{max,abs}$ calcd [nm] | Oscillatory | Most Dominant                      | $\Delta E_{calcd-exp}$ [eV] |
|---------------------|-------|--------------------------------|-------------|------------------------------------|-----------------------------|
| CAM-B3LYP           | S$_6$ | 226.5                          | 5.461       | 0.0575                             | HOMO$\rightarrow$LUMO+4 (65%) |
|                     |       |                                |             |                                    | HOMO$\rightarrow$LUMO+3 (18%) |
|                     | S$_1$ | 354.7                          | 3.487       | 0.9695                             | HOMO$\rightarrow$LUMO (98%)  |
|                     | S$_2$ | 220.5                          | 5.610       | 0.2421                             | HOMO-1$\rightarrow$LUMO (94%) |
|                     | S$_3$ | 209.1                          | 5.914       | 0.0763                             | HOMO$\rightarrow$LUMO+1 (96%) |
|                     | S$_4$ | 202.9                          | 6.096       | 0.003                              | HOMO-1$\rightarrow$LUMO (73%) |
|                     | S$_5$ | 201.0                          | 6.152       | 0.0013                             | HOMO-3$\rightarrow$LUMO (49%) |
|                     | S$_6$ | 189.3                          | 6.535       | 0.0022                             | HOMO-4$\rightarrow$LUMO (83%) |
| CAM-B3LYP (CH$_2$Cl$_2$) | S$_1$ | 377.4                          | 3.277       | 1.0218                             | HOMO$\rightarrow$LUMO (98%)  |
|                     | S$_2$ | 377.4                          | 3.277       | 0.0013                             | HOMO$\rightarrow$LUMO+5 (7%)  |
|                     | S$_3$ | 256.3                          | 5.465       | 0.0013                             | HOMO-1$\rightarrow$LUMO (98%)  |
|                     | S$_4$ | 212.5                          | 5.584       | 0.1968                             | HOMO-1$\rightarrow$LUMO (64%) |
|                     | S$_5$ | 219.7                          | 5.630       | 0.0256                             | HOMO$\rightarrow$LUMO+3 (45%) |
|                     | S$_6$ | 213.9                          | 5.781       | 0.0197                             | HOMO-2$\rightarrow$LUMO (38%) |

$^a$ Gas phase calculation in absence of PCM. $^b$ Employing PCM for dichloromethane as a dielectric continuum. $^c$ Employing a state specific solvation for dichloromethane as a dielectric continuum.

For merocyanine 5b, the longest wavelength band apparently depends on solvent stabilization (Table 4). While gas phase calculations with B3LYP, PBEh1PBE, and CAM-B3LYP functionals predict lowest energy bands of weak intensity dominated by an $n-\pi^*$ (HOMO-1$\rightarrow$LUMO) transition as singlet S$_1$ state, the highest intensity $\pi-\pi^*$ (HOMO$\rightarrow$LUMO) transition represents the S$_2$ state. The solvation effect becomes apparent for all functionals upon employing the implicit PCM for dichloromethane as a continuum, which was actually also used in experimental spectroscopy. For PCM calculations, the lowest energy, highest intensity band predominantly consists of $\pi-\pi^*$ (HOMO$\rightarrow$LUMO) transition, yet, with a minor contribution of the $n-\pi^*$ (HOMO-1$\rightarrow$LUMO) transition in singlet S$_1$ state as shown for the B3LYP with state specific solvation. As seen for all merocyanines 5, emission cannot be detected by the naked eye nor with steady state fluorescence spectroscopy (vide supra).

All TDDFT calculations on merocyanine 5b give higher energies for the lowest energy band than the experimentally determined values by 0.127 to 0.775 eV. Indeed, the smallest deviations are found for the functionals B3LYP (0.127 eV) and PBEh1PBE (0.191 eV) with explicit PCM implementation. These deviations fall into the same range as previously reported for TDDFT calculations on cyanines [45]. The Kohn-Sham frontier molecular orbitals of the B3LYP/6-311++G** PCM calculations nicely illustrate that the intense longest wavelength absorption is dominated by HOMO$\rightarrow$LUMO transition along the chromophore axis (Figure 6, left). The less dominant, weak intensity HOMO-1$\rightarrow$LUMO transition clearly...
possesses n-π* character. In the experiment, this transition might fall in superposition with the broad intense merocyanine π-π* band.

Figure 6. Selected Kohn-Sham frontier molecular orbitals of merocyanine 5b (left) and cyanine 6b (right) (Gaussian 16 B3LYP/6-311++G**, PCM CH₂Cl₂, isosurface value at 0.04) and the calculated HOMO, HOMO-1, and LUMO energies, including the energy differences between the frontier molecular orbitals as well as the calculated and experimentally determined absorption wavelength of merocyanine 5b and cyanine 6b.

Expectedly for cyanine 6b, the PCM solvent implementation predicts the absorption to arise at longer wavelengths in comparison to the gas phase calculations (Table 5). For all exchange correlation hybrid functionals the lowest energy transition is fully represented by HOMO→LUMO transition along the cyanine chromophore axis, as also seen in the Kohn-Sham frontier molecular orbitals (Figure 6, right). As stated above and typical for cyanines, the calculated transition energies for this band are higher and deviate by 0.402 to 0.686 eV in comparison to the experimentally determined absorption energy. As mentioned before, the functionals B3LYP (0.402 eV) and PBEh1PBE (0.451 eV) with explicit PCM implementation possess the smallest deviations.

3. Conclusions

The triflate readily accessible from dimedone is a favorable starting material for consecutive three-component alkynylation-addition sequences to merocyanines with embedded butadiene structure in moderate to excellent yield. Moreover, employing pyrrolidine as an amino component enables a pseudo four-component synthesis of related cyanines by carbonyl condensation of the heterocyclic amine in excellent yield. While butadiene-based (absorption between 360 and 390 nm) and expanded hexatriene (absorption at 442 nm) chromophores are essentially nonfluorescent in solution and in the solid state, the pentamethine cyanines absorb intensively at 443 and 459 nm and also luminesce in solution with low fluorescence quantum yield of 1%. According to TDDFT calculations with various exchange correlation hybrid functionals in the gas phase and in an explicit continuum of dichloromethane, the electronic structure of the longest wavelength absorption bands is highly solvent dependent for both a representative merocyanine and a cyanine. The cyanine typical deviation of calculated transitions to higher energies in comparison to
the experimental data falls in a regime of 0.127 eV for the merocyanine and 0.402 eV for the model cyanine. For merocyanines, the lowest energy absorption band contains n-π* character, which plausibly accounts for the indiscernible luminescence. In contrast, the rigidified cyanine’s lowest energy band is exclusively a π-π* transition and does not interfere with luminescence. The synthetic ease of accessing both merocyanines and cyanines in a one-pot fashion allows for readily preparing substance libraries of both chromophore types, which can be interesting for biophysical analytics. Studies directed to expand the one-pot methodology to bathochromically shifted merocyanines based upon the dimeredone derived trflate are currently underway.

4. Experimental
4.1. 5,5-Dimethyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (2)

In a Schlenk flask with magnetic stir bar, dimeredone (1) (2.80 g, 20.0 mmol) was dissolved in dichloromethane (50 mL) under nitrogen and the solution was cooled to 0 °C (ice water bath) before pyridine (2.00 mL, 24.8 mmol) was added. Trifluoromethanesulfonic anhydride (3.90 mL, 23.2 mmol) was added dropwise to the cooled solution over a period of 1 h. The cooling was stopped and the reaction mixture was stirred at room temp for 2 h. Then, a 1 M aqueous HCl solution (25 mL) was added. The organic layer was washed with a saturated aqueous NaHCO3 solution (3 × 20 mL) and dried (anhydrous Na2SO4). After filtration and removal of the solvents in vacuo, the crude product was purified by flash chromatography on silica gel (n-hexane/ethyl acetate 98:2) to give compound 1 [34] (4.94 g, 91%) as a pale-yellow liquid, Rf (n-hexane/ethyl acetate 20:1): 0.14.

1H NMR (600 MHz, CDCl3): δ 1.13 (s, 6 H), 2.30 (s, 2 H), 2.54 (d, J = 1.3 Hz, 2 H), 6.06 (t, J = 1.3 Hz, 1 H). 13C NMR (151 MHz, CDCl3): δ 28.1 (CH3), 33.5 (Cquat), 42.4 (CH2), 50.6 (CH2), 118.4 (CH), 118.5 (Cquat, q, 1JCF = 321 Hz), 166.1 (Cquat), 197.6 (Cquat). EI MS (70 eV, m/z (%)): 272 (18, [M+]), 244 (15, [C9H11O5SF3]+), 216 (100), 86 (28), 83 (16), 69 (38, [CF3]+), 56 (10), 55 (11), 41 (12).

4.2. General Procedure (GP) for the Three-Component Synthesis of Merocyanines 5 and 8

PdCl2(PPh3)2 (14 mg, 0.02 mmol), Cul (7 mg, 0.04 mmol), compound 2 (272 mg, 1.00 mmol), and dry, degassed THF (1 mL) were placed in a microwave vessel. The solution was saturated with a constant stream of nitrogen through a syringe for 5 min. Then, alkyne 3 (1.0 mmol), K2CO3 (166 mg, 1.20 mmol), or triethylamine (0.14 mL, 1.00 mmol) were added and the mixture was stirred at room temp for 1 h (for experimental details, see Table 6). Then, the amine 4 or Fischer’s base (7) (1.0 mmol) and methanol (1 mL) were added to the reaction mixture. The reaction mixture was then heated in the microwave cavity at 100 °C for 1 h. After cooling to room temp, the solvents were removed under reduced pressure and the residue was purified by flash chromatography on silica gel (n-hexane/ethyl acetate) to give the analytically pure product merocyanine 5 and 8.

| Entry | Alkyne 3 | Amine 4 or Fischer’s Base (7) | Yield of Merocyanines 5 and 8 |
|-------|----------|-------------------------------|-----------------------------|
| 1a    | 140 µL (1.00 mmol) of 3a | 90 µL (1.00 mmol) of 4a | 135 mg (65%) of 5a |
| 2b    | 140 µL (1.00 mmol) of 3a | 90 µL (1.00 mmol) of 4a | 82 mg (35%) of 5a |
| 3a    | 140 µL (1.00 mmol) of 3a | 85 µL (1.00 mmol) of 4c | 71 mg (53%) of 5b |
| 4a    | 110 µL (1.00 mmol) of 3d | 90 µL (1.00 mmol) of 4a | 171 mg (55%) of 5c |
| 5b    | 110 µL (1.00 mmol) of 3d | 90 µL (1.00 mmol) of 4a | 212 mg (68%) of 5c |
| 6a    | 110 µL (1.00 mmol) of 3d | 100 µL (1.00 mmol) of 4b | 191 mg (62%) of 5d |
| 7b    | 110 µL (1.00 mmol) of 3d | 100 µL (1.00 mmol) of 4b | 62 mg (20%) of 5d |
| 8b    | 110 µL (1.00 mmol) of 3d | 85 µL (1.00 mmol) of 4c | 118 mg (40%) of 5e |
| 9b    | 140 µL (1.00 mmol) of 3a | 180 µL (1.00 mmol) of 1,3,3-trimethyl-2-methylenindoline (7) | 21 mg (7%) of 8 |

a The reaction was performed with K2CO3 as a base. b The reaction was performed with NEt3 as a base.
4.3. (E)-5,5-Dimethyl-3-(2-morpholinovinyl)cyclohex-2-en-1-one (5a)

According to the GP and after chromatography on silica gel (n-hexane/ethyl acetate 2:1) and drying under vacuum, compound 5a (135 mg, 65%, with potassium carbonate as a base; 82 mg, 35%, with triethylamine as a base) was obtained as an orange solid, mp 72 °C, Rf (n-hexane/ethyl acetate 2:1): 0.12.

1H NMR (600 MHz, MeOD-d₄): δ 1.08 (s, 6 H), 2.22 (s, 2 H), 2.43 (s, 2 H), 3.34 (t, J = 4.7 Hz, 4 H), 3.73 (t, J = 4.9 Hz, 4 H), 5.43 (d, J = 13.5 Hz, 1 H), 5.71 (s, 1 H), 7.15 (d, J = 13.5 Hz, 1 H). 13C NMR (151 MHz, MeOD-d₄): δ 28.5 (CH₃), 34.0 (Cquat), 40.2 (CH₂), 49.7 (CH₂), 51.4 (CH₂), 67.2 (CH), 100.4 (CH), 116.3 (CH), 148.0 (CH), 164.4 (Cquat), 209.0 (Cquat). El MS (70 eV, m/z (%)): 236 (18), 235 (100, [M⁺]), 222 (10), 221 (11), 220 (31, [C₁₃H₁₅NO₂⁺]), 214 (15), 207 (19, [C₁₂H₁₇NO₂⁺]), 206 (16), 192 (22), 179 (13, [C₁₀H₁₃NO⁺]), 178 (31), 153 (12), 152 (13), 151 (15, [C₉H₁₃NO⁺]), 150 (18), 149 (20, [C₁₀H₁₅O⁺]), 138 (19, [C₈H₁₂NO⁺]), 136 (48, [C₇H₁₂O⁺]), 135 (11), 122 (20), 121 (41), 120 (13), 112 (12, [C₇H₁₉NO⁺]), 107 (16), 106 (11), 105 (15), 100 (11), 94 (17), 93 (56), 91 (11), 86 (17, [C₄H₆O⁺]), 85 (20), 79 (14), 77 (14), 67 (14), 65 (12), 57 (10), 56 (14), 55 (21), 42 (10), 41 (13). IR: ν [cm⁻¹]: 3053 (w), 3026 (w), 2955 (w), 2926 (w), 2891 (w), 2864 (w), 1589 (s), 1533 (s), 1504 (w), 1443 (m), 1422 (m), 1412 (m), 1375 (m), 1319 (m), 1298 (m), 1277 (s), 1252 (m), 1227 (m), 1194 (m), 1152 (m), 1109 (s), 1069 (m), 1047 (w), 1020 (m), 995 (m), 943 (m), 924 (w), 854 (m), 822 (w), 799 (w), 756 (w), 745 (w), 725 (w), 681 (m), 602 (m). Anal calcd for C₁₄H₂₁NO₂ (235.3): C 71.46, H 8.99, N 5.95; Found: C 71.27, H 9.28, N 5.93.

4.4. (E)-5,5-Dimethyl-3-[2-(pyrrolidin-1-yl)vinyl]cyclohex-2-en-1-one (5b)

According to the GP and after chromatography on silica gel (n-hexane/ethyl acetate 3:1) and drying under vacuum, compound 5b (116 mg, 53%) was obtained as a yellow solid, mp 125 °C, Rf (n-hexane/ethyl acetate/NEt₃ 200:100:3): 0.14.

1H NMR (600 MHz, CDCl₃): δ 1.04 (s, 6 H), 1.94 (t, J = 6.6 Hz, 4 H), 2.20 (s, 2 H), 2.27 (s, 2 H), 3.30 (t, J = 6.7 Hz, 4 H), 5.04 (d, J = 13.4 Hz, 1 H), 5.70 (s, 1 H), 7.08 (d, J = 13.3 Hz, 1 H). 13C NMR (151 MHz, CDCl₃): δ 25.1 (CH₂), 28.5 (CH₃), 33.0 (Cquat), 39.6 (CH₂), 49.1 (CH₂), 50.9 (CH₂), 99.2 (CH), 116.2 (CH), 141.4 (CH), 158.9 (Cquat), 198.3 (Cquat). El MS (70 eV, m/z (%)): 220 (19), 219 (100, [M⁺]), 204 (55, [C₁₃H₁₇NO⁺]), 191 (11, [C₁₂H₁₅O⁺]), 190 (16), 176 (23), 163 (10, [C₁₀H₁₅NO⁺]), 162 (20), 136 (17, [C₁₀H₂₀O⁺]), 135 (42, [C₉H₁₉NO⁺]), 134 (86), 122 (13, [C₈H₁₄N₂⁺]), 121 (10), 120 (43), 107 (59), 106 (16), 93 (12), 79 (11), 70 (10, [C₄H₆N₂⁺]).

IR: ν [cm⁻¹]: 3051 (w), 3013 (w), 2990 (w), 2981 (w), 2891 (w), 2864 (w), 1589 (s), 1533 (s), 1504 (w), 1443 (m), 1422 (m), 1412 (m), 1375 (m), 1319 (m), 1298 (m), 1277 (s), 1252 (m), 1227 (m), 1194 (m), 1152 (m), 1109 (s), 1069 (m), 1047 (w), 1020 (m), 995 (m), 943 (m), 924 (w), 854 (m), 822 (w), 799 (w), 756 (w), 745 (w), 725 (w), 681 (m), 602 (m). Anal calcd for C₁₄H₂₁NO (219.3): C 76.67, H 9.65, N 6.39; Found: C 76.43, H 9.94, N 6.17.

4.5. (E)-5,5-Dimethyl-3-(2-phenylvinyl)cyclohex-2-en-1-one (5c)

According to the GP and after chromatography on silica gel (n-hexane/ethyl acetate 3:1) and drying under vacuum, compound 5c (171 mg, 55%, with potassium carbonate as a base; 212 mg, 68%, with triethylamine as a base) was obtained as an yellow solid, mp 78 °C, Rf (n-hexane/ethyl acetate 3:1): 0.09.

1H NMR (600 MHz, DMSO-d₆): δ 0.76 (s, 6 H), 1.75 (s, 2 H), 1.92 (s, 2 H), 2.94 (t, J = 4.8 Hz, 4 H), 3.60 (t, J = 4.8 Hz, 4 H), 5.30 (s, 1 H), 5.28 (s, 1 H), 7.16–7.32 (m, 2 H), 7.37–7.48 (m, 3 H). 13C NMR (151 MHz, DMSO-d₆): δ 27.8 (CH₃), 32.9 (Cquat), 43.4 (CH₂), 48.3 (CH₂), 50.3 (CH₂), 65.8 (CH₂), 103.9 (CH), 121.1 (CH), 128.8 (CH), 129.3 (CH), 129.4 (CH), 136.4 (Cquat), 156.2 (Cquat), 157.9 (Cquat), 196.9 (Cquat). El MS (70 eV, m/z (%)): 312 (22), 311 (100, [M⁺]), 310 (26), 299 (11, [C₁₉H₂₂NO₂⁺]), 295 (17), 294 (76), 254 (19), 252 (11), 227 (14, [C₁₅H₁₇NO⁺]), 226 (13), 225 (21, [C₁₄H₁₇O⁺]), 212 (32), 198 (11), 196 (12), 170 (11), 169 (4), 168 (15), 141 (15), 105 (60), 77 (17, [C₈H₆⁺]), 43 (11). IR: ν [cm⁻¹]: 3030 (w), 2963 (w), 2932 (w), 2913 (w), 2899 (w), 2855 (w), 2822 (w), 1639 (m), 1579 (m), 1570 (s), 77
1557 (m), 1539 (m), 1537 (s), 1534 (s), 1522 (m), 1518 (m), 1508 (m), 1491 (w), 1462 (w), 1449 (m), 1077 (w), 1069 (m), 1030 (m), 1020 (m), 999 (w), 941 (s), 932 (s), 903 (w), 889 (m), 883 (m), 3.15 (t, CH₂), 129.7 (CH₃), 137.6 (C₃H₇), 129.0 (CH₂), 129.7 (CH₃), 137.6 (C₃H₇), 157.7 (C₃H₇), 159.9 (C₃H₇), 198.6 (C₃H₇). El MS (70 eV, m/z (%)): 310 (15), 309 (68, [M⁺]), 308 (28), 294 (10, [C₃H₂NO⁺]), 293 (16), 292 (68), 280 (11, [C₃H₁₂NO⁺]), 253 (10, [C₁₇H₁₉NO⁺]), 252 (41), 225 (19, [C₁₆H₁₇NO⁺]), 224 (29), 211 (20), 210 (100), [C₁₅H₁₁O⁺], 196 (10), 170 (13), 115 (11), 105 (12), 104 (10), 84 (14, [C₃H₁₀NO⁺]). IR: v cm⁻¹: 2988 (w), 2936 (w), 2864 (w), 2828 (w), 1628 (m), 1576 (w), 1561 (m), 1551 (s), 1546 (s), 1541 (s), 1534 (s), 1522 (m), 1518 (m), 1508 (m), 1491 (w), 1462 (w), 1449 (m), 1441 (m), 1420 (w), 1370 (m), 1364 (m), 1302 (m), 1279 (m), 1263 (w), 1227 (s), 1202 (m), 1157 (w), 1138 (m), 1119 (m), 1101 (s), 1070 (w), 1028 (w), 1007 (w), 918 (w), 895 (m), 880 (m), 860 (m), 851 (m), 831 (w), 818 (w), 797 (w), 777 (s), 725 (m), 702 (m), 675 (m), 638 (w), 606 (m). UV/Vis (CH₂Cl₂): λmax [nm] (ε [Lcm⁻¹mol⁻¹]): 383 (22000). HRMS (ESI, m/z (%)) calcd for [C₃H₂NO⁺]: 310.2165 (100), 311.2199 (23), 312.2233 (3); Found: 310.2170 (100), 311.2201 (19), 312.2231 (3).

4.7. (E)-5,5-Dimethyl-3-[2-phenyl-2-(pyrrolidin-1-yl)vinyl]cyclohex-2-en-1-one (5e)

According to the GP and after chromatography on silica gel (n-hexane/ethyl acetate/Nεt₃ 500:100:6) and drying under vacuum, compound 5e (118 mg, 40%) was obtained as an orange solid, mp 133 °C, Rₜ (n-hexane/ethyl acetate/Nεt₃ 200:100:3): 0.17.

1H NMR (600 MHz, CDCl₃): δ 0.78 (s, 6 H), 1.65 (s, 2 H), 1.89 (t, J = 6.7 Hz, 4 H), 2.01 (s, 2 H), 3.15 (t, J = 6.3 Hz, 4 H), 5.05 (s, 1 H), 5.41 (s, 1 H), 5.19–7.25 (m, 2 H), 7.35–7.47 (m, 3 H), 1.37 (CH₂), 18.4 (CH₂), 22.8 (CH₂), 33.2 (C₃H₇), 44.0 (C₃H₇), 49.2 (CH₂), 50.7 (CH₂), 100.2 (CH₂), 118.4 (CH), 126.8 (CH), 129.7 (CH), 137.9 (C₃H₇), 154.9 (C₃H₇), 159.8 (C₃H₇), 198.6 (C₃H₇). El MS (70 eV, m/z (%)): 296 (15, 295 (73, [M⁺]), 294 (24), 280 (34, [C₁₇H₂₂NO⁺]), 279 (21), 278 (94), 239 (11, [C₁₆H₁₇NO⁺]), 238 (32), 211 (18, [C₁₅H₁₇N⁺]), 210 (31), 197 (21, [C₁₄H₁₅N⁺]), 196 (100), 183 (10), 182 (15), 170 (12), 168 (11), 167 (10), 142 (10), 141 (17), 115 (13), 105 (11). IR: v cm⁻¹: 3057 (w), 2945 (w), 2978 (w), 2864 (w), 2834 (w), 1620 (m), 1533 (s), 1501 (m), 1474 (m), 1453 (m), 1445 (m), 1425 (m), 1366 (s), 1344 (m), 1315 (m), 1302 (s), 1279 (s), 1254 (m), 1299 (m), 1204 (s), 1179 (m), 1165 (m), 1140 (s), 1109 (s), 1074 (m), 1028 (w), 991 (m), 970 (w), 937 (w), 924 (m), 893 (m), 885 (m), 876 (s), 864 (m), 804 (w), 775 (s), 743 (w), 706 (s), 691 (m), 673 (w), 631 (w). UV/Vis (CH₂Cl₂): λmax [nm] (ε [Lcm⁻¹mol⁻¹]): 388 (43000). Anal calcd for C₃₀H₂₅NO (295.4): C 81.31, H 8.53, N 4.74; Found: C 81.02, H 8.80, N 4.58.

4.8. 5,5-Dimethyl-3-(E)-(E)-1,3,3-trimethylindolin-2-yldien)prop-1-en-1-yl)cyclohex-2-en-1-one (8)

According to the GP and after chromatography on silica gel (n-hexane/ethyl acetate/Nεt₃ 300:100:4) and drying under vacuum, compound 8 (21 mg, 7%) was obtained as an orange solid, mp 86 °C, Rₜ (n-hexane/ethyl acetate/Nεt₃ 300:100:4): 0.31.
1H NMR (600 MHz, CDCl3): δ 1.10 (s, 6 H), 1.61 (s, 6 H), 2.27 (s, 2 H), 2.39 (s, 2 H), 3.15 (s, 3 H), 5.42 (d, J = 12.0 Hz, 1 H), 5.90 (s, 1 H), 6.11 (d, J = 14.6 Hz, 1 H), 6.66 (d, J = 7.8 Hz, 1 H), 6.89 (t, J = 7.4 Hz, 1 H), 7.13–7.21 (m, 2 H), 7.30 (dd, J = 14.8, 12.0 Hz, 1 H). 13C NMR (151 MHz, CDCl3): δ 28.7 (CH2), 28.8 (CH3), 29.3 (CH3), 33.4 (quat), 39.7 (CH2), 46.1 (quat), 51.5 (CH2), 96.5 (CH), 106.6 (CH), 120.4 (CH), 121.7 (CH), 122.3 (CH), 124.6 (CH), 128.0 (CH), 132.9 (CH), 138.9 (quat), 144.8 (quat), 156.9 (quat), 160.8 (quat), 199.9 (quat). IR: υ [cm⁻¹]: 3049 (w), 2955 (w), 2924 (w), 2864 (w), 1641 (w), 1618 (m), 1595 (m), 1576 (m), 1541 (s), 1537 (s), 1489 (m), 1456 (m), 1375 (m), 1364 (m), 1350 (m), 1339 (m), 1314 (m), 1300 (m), 1273 (s), 1246 (m), 1204 (m), 1182 (m), 1165 (m), 1148 (s), 1115 (s), 1078 (m), 1042 (w), 1020 (m), 993 (w), 959 (m), 930 (m), 897 (w), 878 (m), 858 (m), 831 (w), 797 (m), 741 (s), 716 (w), 656 (w), 637 (w), 604 (w). UV/Vis (CH2Cl2): λmax [nm] (ε [Lcm⁻¹mol⁻¹]): 275 (14000), 442 (27000). HRMS (ESI, calcd for [C22H28NO]+: 322.2165 (100), 323.2199 (24), 324.2233 (3); Found: 322.2169 (100), 323.2203 (18), 324.2289 (3).

4.9. General Procedure (GP) for the Pseudo Four-Component Synthesis of Cyanines 6

PdCl2(PPh3)2 (14 mg, 0.02 mmol), CuI (7 mg, 0.04 mmol), compound 13 (272 mg, 1.00 mmol), and dry, degassed THF (1 mL) were placed in a microwave vessel. The solution was saturated with a constant stream of nitrogen through a syringe for 5 min. Then, alkyne 7 (1.0 mmol) and triethylamine (0.14 mL, 1.00 mmol) were added and the mixture was stirred at room temp for 1 h (for experimental details, see Table 7). Then, the pyrrolidine (9c) (1.0 mmol) and methanol (1 mL) were added to the reaction mixture. The reaction mixture was then heated in the microwave cavity at 100 °C for 1 h. After cooling to room temp the solvents were removed under reduced pressure and the residue was purified by flash chromatography on silica gel (n-hexane/ethyl acetate) to give the analytically pure product 6.

Table 7. Experimental details of the consecutive pseudo four-component synthesis of cyanines 6.

| Entry | Alkyne 7 | Amine 9c | Yield * |
|-------|---------|---------|---------|
| 1     | 140 µL  (0.98 mmol) of 7a | 85 µL (1.00 mmol) of 9c | 209 mg (99%) of 6b |
| 2     | 110 µL  (1.00 mmol) of 7d | 85 µL (1.00 mmol) of 9c | 214 mg (86%) of 6c |

* The yield refers to the employed amount of amine, i.e., two equivs of amine 9c reacted with one equiv of compound 2. The unreacted alkyne intermediate was not isolated.

4.10. (E)-1-(5,5-Dimethyl-3-[2-(pyrrolidin-1-yl)vinyl]cyclohex-2-en-1-ylidene)pyrrolidin-1-ium (6b)

According to the GP, upon reaction of alkyne 7a (140 µL, 0.98 mmol) and pyrrolidine (9c) (85 µL, 1.00 mmol) and chromatography on silica gel (n-hexane/ethyl acetate/Net3: 200:100:3) and drying under vacuum, compound 6b (209 mg, 99%) was obtained as an orange solid, mp 180–200:100:3 and 99% yield.
(2). IR: $\nu$ [cm$^{-1}$]: 2984 (w), 2957 (w), 2872 (w), 1624 (w), 1522 (m), 1477 (w), 1441 (m), 1412 (m), 1396 (w), 1375 (m), 1348 (m), 1337 (w), 1325 (w), 1262 (s), 1248 (s), 1233 (m), 1221 (s), 1152 (s), 1103 (m), 1026 (s), 1005 (w), 986 (w), 966 (w), 947 (w), 924 (w), 912 (w), 883 (m), 876 (m), 853 (m), 781 (w), 766 (w), 754 (w), 706 (w), 633 (s). UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ [nm] ($\epsilon$ [L·cm$^{-1}$·mol$^{-1}$]): 443 (114000). Emission (CH$_2$Cl$_2$): $\lambda_{max}$ [nm]: 459. Stokes shift [cm$^{-1}$]: 800. Anal calcd for C$_{10}$H$_{20}$F$_3$N$_2$O$_3$S (422.5): C 54.01, H 6.92, N 6.63, S 7.59; Found: C 54.04, H 7.21, N 5.64, S 7.48.

4.11. $\epsilon$-1-(5,5-Dimethyl-3-[2-phenyl-2-(pyrrolidin-1-yl)vinyl]cyclohex-2-en-1-yldien)pyrrolidin-1-ium (6c)

According to the GP, upon reaction of alkyne 7d (110 $\mu$L, 1.00 mmol) and pyrrolidine (9c) (85 $\mu$L, 1.00 mmol) and after chromatography on silica gel (n-hexane/ethyle acetate/NET$_3$ 200:100:3) and drying under vacuum, compound 6c (214 mg, 86%) was obtained as an orange solid, mp 147 $^\circ$C, $R_f$ (ethyl acetate/MeOH 3:1): 0.07.

$^1$H NMR (600 MHz, DMSO-d$_6$): $\delta$ 0.83 (s, 6 H), 1.94 (s, 2 H), 2.00–2.04 (m, 2 H), 2.33 (s, 2 H), 2.91 (s, 2 H), 3.19 (t, $J$ = 7.9 Hz, 2 H), 3.48–3.53 (m, 2 H), 3.60 (t, $J$ = 7.7 Hz, 2 H), 5.11 (s, 1 H), 5.52 (s, 1 H), 7.34–7.38 (m, 2 H), 7.45–7.78 (m, 3 H).

$^1$H NMR (600 MHz, DMSO-d$_6$): $\delta$ 0.90 (s, 6 H), 1.89–1.96 (m, 6 H), 2.06–2.07 (m, 1 H), 2.08–2.09 (m, 1 H), 2.10–2.14 (m, 2 H), 2.41 (s, 2 H), 2.99 (s, 2 H), 3.28–3.36 (m, 2 H), 3.61–3.65 (m, 2 H), 3.65–3.73 (m, 2 H), 5.19 (s, 1 H), 5.57 (s, 1 H), 7.40–7.44 (m, 2 H), 7.58–7.66 (m, 3 H).

$^1$H NMR (600 MHz, DMSO-d$_6$): $\delta$ 0.89 (s, 6 H), 1.91 (q, $J$ = 6.9 Hz, 6 H), 2.08–2.14 (m, 3 H), 2.40 (s, 2 H), 3.14 (s, 3 H), 3.24–3.38 (m, 2 H), 3.62 (s, 2 H), 3.67 (t, $J$ = 7.0 Hz, 2 H), 4.66 (s, 1 H), 5.15–6.24 (m, 1 H), 7.37–7.49 (m, 2 H), 7.56–7.70 (m, 3 H).

$^{13}$C NMR (151 MHz, DMSO-d$_6$): $\delta$ 24.0 (CH$_3$), 24.3 (CH$_2$), 24.6 (CH$_2$), 24.7 (CH$_2$), 27.3 (CH$_3$), 31.5 (C$_{quat}$), 40.9 (CH$_3$), 48.9 (C$_{quat}$), 49.3 (CH$_2$), 49.7 (CH$_2$), 51.4 (CH$_2$), 120.7 (C$_{quat}$, d, $J_{C-F}$ = 322 Hz), 127.2 (CH), 127.2 (CH), 129.7 (CH), 129.9 (CH), 136.4 (C$_{quat}$), 162.5 (C$_{quat}$), 163.5 (C$_{quat}$).

$^{13}$C NMR (151 MHz, DMSO-d$_6$): $\delta$ 24.0 (CH$_3$), 24.3 (CH$_2$), 24.6 (CH$_2$), 24.7 (CH$_2$), 27.3 (CH$_3$), 31.5 (C$_{quat}$), 40.9 (CH$_3$), 48.9 (C$_{quat}$), 49.3 (CH$_2$), 49.7 (CH$_2$), 51.4 (CH$_2$), 120.7 (C$_{quat}$, d, $J_{C-F}$ = 322 Hz), 127.2 (CH), 127.2 (CH), 129.7 (CH), 129.9 (CH), 136.4 (C$_{quat}$), 162.5 (C$_{quat}$), 163.5 (C$_{quat}$).

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/photchem2030044/s1. Figure S1: Three kinds of helix chains constitute the channel column of NUM-14. Figure S2: Comparison of simulated, experimental, and activated PXRD patterns of NUM-14. Figure S3. TGA curve for NUM-14 under Ar atmosphere. Figure S4: The PXRD patterns for NUM-14 after immersed in common solvents a week. Figure S5. The details of Virial equation (solid lines) fitting to the experimental CO$_2$ adsorption data (symbols) for NUM-14a. Figure S6: The details of Virial equation (solid lines) fitting to the experimental CO$_2$ adsorption data (symbols) for NUM-14a. Figure S7: The details of Virial equation (solid lines) fitting to the experimental CO$_2$ adsorption data (symbols) for NUM-14a at 273 K. Figure S9: The details of dual-site Langmuir-Freundlich isotherm (solid lines) fitting to the experimental CO$_2$ adsorption data (symbols) for NUM-14a at 273 K.
experimental C₂H₂ adsorption data (symbols) for NUM-14a at 298 K. Figure S10: The details of single-site Langmuir-Freundlich isotherm (solid lines) fitting to the experimental CO₂ adsorption data (symbols) for NUM-14a at 273 K. Figure S11: The details of single-site Langmuir-Freundlich isotherm (solid lines) fitting to the experimental CO₂ adsorption data (symbols) for NUM-14a at 298 K. Figure S12: The details of dual-site Langmuir-Freundlich isotherm (solid lines) fitting to the experimental C₂H₄ adsorption data (symbols) for NUM-14a at 273 K. Figure S13: The details of dual-site Langmuir-Freundlich isotherm (solid lines) fitting to the experimental C₂H₄ adsorption data (symbols) for NUM-14a at 298 K. Table S1: Crystal data and structure refinement parameters for NUM-14 [46–49].

Author Contributions: The work consists of parts of the Ph.D. thesis of J.P., which is supervised by T.J.J.M. and the B.Sc. thesis of T.G., which was supervised by J.P. The conceptualization was outlined and accompanied by T.J.J.M. Synthetic studies were performed by J.P. and T.G. All analytical assignments and photophysical investigations were performed by J.P. The crystal structure analysis was performed and solved by G.J.R. The DFT and TDDFT computations and interpretations were performed by B.M. Writing—original draft preparation, J.P.; writing—review and editing, T.J.J.M.; project administration and funding acquisition was done by T.J.J.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Deutsche Forschungsgemeinschaft (Mu 1088/9-1) and the Fonds der Chemischen Industrie.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data (spectra and computational input files) are collected in the Supplementary Materials of this article.

Acknowledgments: We cordially thank the Deutsche Forschungsgemeinschaft (Mu 1088/9-1) and the Fonds der Chemischen Industrie for financial support. Computational support and infrastructure were provided by the “Centre for Information and Media Technology” (ZIM) at the University of Düsseldorf (Germany). We thank CeMSA@HHU (Center for Molecular and Structural Analytics @ Heinrich Heine University) for recording the mass-spectrometric and the NMR-spectroscopic data.

Conflicts of Interest: The authors declare no conflict of interest.

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