Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Unraveling the structure and exciton coupling for multichromophoric merocyanine dye molecules in solution

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Table of Contents

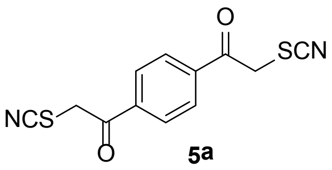
1. Materials and methods

All solvents and reagents were purchased from commercial sources and used as received without further purification, unless otherwise stated. Column chromatography was performed using silica gel 60M (0.04 – 0.063 mm) from Macherey-Nagel. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Advance 400 or Bruker Advance DMX 600 and calibrated to the residual solvent peak. All chemical shifts δ are in ppm. High-resolution mass spectra (ESI) were recorded on an ESI MicrOTOF Focus spectrometer from Bruker Daltonics. MALDI-TOF mass spectra were recorded on a Bruker Daltronik GmbH (Autoflex II) mass spectrometer. Elemental analyses were performed with an Elementar vario micro cube instrument. For all spectroscopic measurements, spectroscopic grade solvents (Uvasol) from Merck (Hohenbrunn, Germany) were used. UV-Vis spectra of the synthesized compounds were recorded on Perkin Elmer UV-Vis spectrometers Lambda 950, Lambda 35, or Lambda 40P in conventional quartz cell cuvettes with path lengths of 1 – 20 mm**.** Melting points were determined on Olympus BX41 optical microscope with heating stage and are uncorrected.

2. Synthesis

1,1'-(1,4-Phenylene)-bis(2-thiocyanatoethanone) **5a**:

A 100 mL ethanol solution of **6a** (5.00 g, 15.6 mmol; 1 equiv.) and sodium thiocyanate (2.78 g, 34.4 mmol; 2.2 equiv.) was refluxed for 20 h. After being cooled down to room temperature, the precipitate was separated by filtration, washed with water, and recrystallized from acetone to afford compound **5a** as a yellow-brown solid. Yield: 1.89 g (6.84 mmol, 44%).

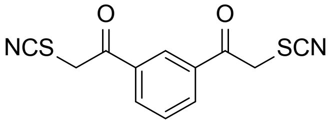


5a

Mp.: 160 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ = 8.26 (s, 4H), 5.14 (s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 192.2, 138.1, 129.0, 112.7, 41.8. HRMS (ESI, positive, acetonitrile): *m/z* 294.0365 [*M*+NH$_4$]$^+$, calculated for $C_{12}H_{12}N_3O_2S_2$: 294.0365.

1,1'-(1,3-Phenylene)-bis(2-thiocyanatoethanone) **5b**:

A 100 mL ethanol solution of **6b** (9.00 g, 28.1 mmol; 1 equiv.) and sodium thiocyanate (5.02 g, 61.9 mmol; 2.2 equiv.) was refluxed for 20 h. After addition of 100 mL water and 300 mL ethyl acetate the organic phase was separated, dried over $MgSO_4$ and the solvent was distilled off. Target compound **5b** was obtained as a brown solid after recrystallization from ethyl acetate, washing twice with 3 mL ethanol and drying under vacuum. Yield: 3.01 g (10.9 mmol, 39%).

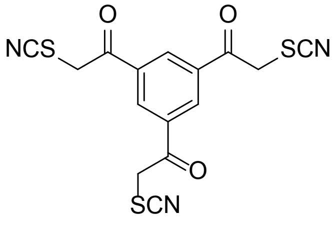


5b

Mp.: 127–129 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.50 (t, J = 1.8 Hz, 1H), 8.23 (dd, J = 7.8 Hz, J = 1.8 Hz, 2H), 7.66 (t, J = 8.0 Hz, 1H), 4.75 (s, 4H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 190.5, 135.3, 134.3, 130.6, 128.6, 111.6, 42.8. HRMS (ESI, negative, acetonitrile): *m/z* 274.9952 [*M*–H]$^-$, calculated for $C_{12}H_7N_2O_2S_2$: 274.9954.

1,1',1''-(1,3,5-Phenylene)-tris(2-thiocyanatoethanone) **5c**:

A 100 mL ethanol solution of **6c** (7.24 g, 16.4 mmol; 1 equiv.) and sodium thiocyanate (4.38 g, 54.1 mmol; 3.2 equiv.) was refluxed for 4 h. After cooling down to room temperature the precipitate was separated by filtration, washed with water and dried under vacuum at 60 °C to obtain compound **5c** as a yellow-brown solid. Yield: 4.48 g (11.9 mmol, 73%).

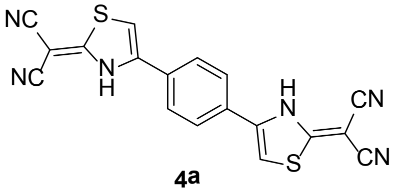


5c

Mp.: > 205 °C (decomposition). ^{1}H NMR (400 MHz, acetone-d_6): δ = 8.97 (s, 3H), 5.23 (s, 6H). ^{13}C NMR (101 MHz, acetone-d_6): δ = 191.6, 137.0, 133.8, 112.2, 42.9. HRMS (ESI, positive, acetone): *m/z* 375.9880 [*M*+H]$^+$, calculated for $C_{15}H_{10}N_3O_3S_3$: 375.9879.

2,2'-(4,4'-(1,4-Phenylene)-bis(thiazole-4(3*H*)-yl-2(3*H*)-ylidene))dimalononitrile **4a**:

To a 20 mL ethanol suspension of **5a** (870 mg, 3.15 mmol; 1 equiv.) and malononitrile (416 mg, 6.30 mmol; 2 equiv.) at 30 °C was slowly added trimethylamine (1.91 g, 18.9 mmol) and afterwards stirred for 20 h. After addition of 15 mL water and adjustment of pH = 1 with HCl, the precipitation was separated by filtration, washed with water and dried under vacuum. Product **4a** was obtained as a brown solid. Yield: 1.11 g (2.98 mmol, 95%).

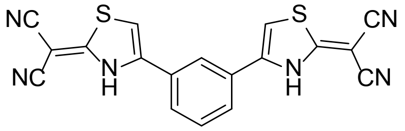


4a

Mp.: > 145 °C (decomposition). ^{1}H NMR (400 MHz, MeOD-d_4): δ = 7.87 (s, 4H), 7.11 (s, 2H). MS (EI): *m/z* 372.1 [M]$^+$, calculated for $C_{18}H_8N_6S_2$: 372.0.

2,2'-(4,4'-(1,3-Phenylene)-bis(thiazole-4(3*H*)-yl-2(3*H*)-ylidene))dimalononitrile **4b**:

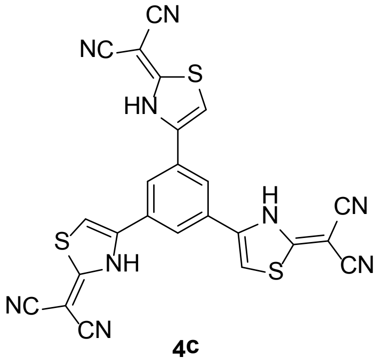
To a 60 mL ethanol suspension of **5b** (1.72 g, 6.22 mmol; 1 equiv.) and malononitrile (820 mg, 12.4 mmol; 2 equiv.) at 30 °C was slowly added trimethylamine (3.76 g, 37.2 mmol) and afterwards stirred for 20 h. After addition of 40 mL water and adjustment of pH = 1 with HCl, the precipitate was separated by filtration, washed with water and dried under vacuum. Product **4b** was obtained as a brown solid. Yield: 2.32 g (6.22 mmol, 99%).



4b

Mp.: > 183 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ= 8.06 (s, 1H), 7.78 (dd, J = 7.8 Hz, J = 1.7 Hz, 2H), 7.58 (t, J = 7.8 Hz, 1H), 7.43 (s, 2H). MS (EI): *m/z* 300.0 [M−CN$_2$S]$^+$, calculated for $C_{17}H_8N_4S$: 300.0.

2,2',2''-(4,4',4''-(1,3,5-Phenylene)-tris(thiazole-4(3*H*)-yl-2(3*H*)-ylidene))trimalononitrile **4c**: To a 100 mL ethanol suspension of **5c** (4.00 g, 10.7 mmol; 1 equiv.) and malononitrile (2.11 g, 31.9 mmol; 3 equiv.) at 30 °C was slowly added trimethylamine (9.70 g, 95.9 mmol) and afterwards stirred for 20 h. After addition of 20 mL water and adjustment of pH = 1 with HCl, the precipitate was separated by filtration, washed with water and dried under vacuum. Product **4c** was obtained as a brown solid. Yield: 5.51 g (10.6 mmol, 99%).

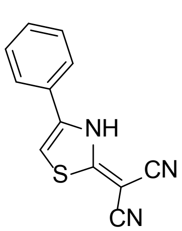


4c

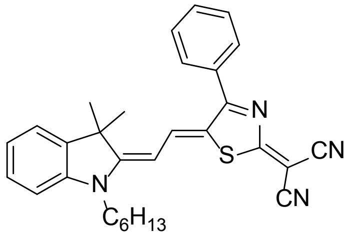
Mp.: > 150 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ= 9.80 (bs, 3H), 8.09 (s, 3H), 7.50 (s, 3H). MS (MALDI): *m/z* 441.39 [M-(CN)$_3$]$^+$, calculated for $C_{21}H_9N_6S_3$: 441.01.

2-{(*Z*)-5-[(*E*)-2-(1-Hexyl-3,3-dimethylindolin-2-ylidene)ethylidene]-4-phenylthiazol-2(5*H*)-ylidene}malononitrile **1**:

This compound was reported previously but no characterization data are available.[1] A solution of phenylthiazole derivative **4d**[1,2] (451 mg, 2.00 mmol; 1 equiv.) and **8** (543 mg, 2.00 mmol; 1 equiv.) in 2 mL acetic anhydride was heated to 90 °C for 60 min. After cooling down to room temperature, *iso*-propanol was added and the precipitate separated by filtration, washed with *n*-hexane and subsequently purified by column chromatography (CH_2Cl_2/MeOH 100 : 1 v/v). After recrystallization from CH_2Cl_2/*n*-hexane a blue solid was obtained. Yield: 410 mg (857 µmol, 43%).



4d

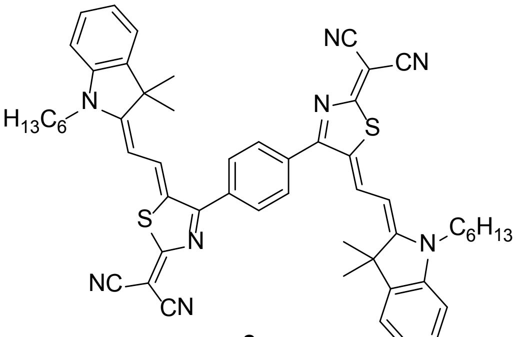


1

Mp.: 281–282 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 8.01$ (d, $J = 13.8$ Hz, 1H), 7.76–7.71 (m, 2H), 7.64–7.56 (m, 3H), 7.43–7.38 (m, 1H), 7.37–7.34 (m, 1H), 7.26 (td, $J = 7.4$ Hz, $J = 0.9$ Hz, 1H), 7.11 (d, $J = 8.1$ Hz, 1H), 5.86 (d, $J = 13.8$ Hz, 1H), 3.97 (t, $J = 7.6$ Hz, 2H), 1.86–1.77 (m, 2H), 1.54 (s, 6H), 1.50–1.29 (m, 6H), 0.92 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2): $\delta = 180.3$, 174.34, 174.30, 142.4, 141.5, 141.1, 133.6, 131.4, 130.0, 129.3, 129.2, 127.2, 126.0, 122.7, 118.6, 116.3, 111.2, 101.0, 49.8, 45.0, 31.8, 28.0, 27.6, 27.0, 22.9, 14.1. HRMS (ESI, positive, acetonitrile / chloroform): *m/z* 478.2186 $[M]^+$, calculated for $C_{30}H_{30}N_4S$: 478.2185. UV-Vis (CH_2Cl_2): λ_{max} (ε) = 633 nm (118000 L mol^{-1} cm^{-1}). Elemental analysis (%): calculated for $C_{30}H_{30}N_4S$: C, 75.28; H, 6.32; N, 11.71; S, 6.70; found: C, 75.12; H, 6.47; N, 11.71; S, 6.70.

1,4-Phenylene-bis(merocyanine) **2p**:

A solution of **4a** (243 mg, 652 µmol; 1 equiv.) and **8** (375 mg, 1.38 mmol; 2.1 equiv.) in 2 mL acetic anhydride was heated to 90 °C for 30 min. After cooling down to room temperature, *iso*-propanol was added and the precipitate separated by filtration, washed with toluene and *n*-hexane and subsequently purified by column chromatography (CH_2Cl_2/MeOH 100 : 3 v/v). After recrystallization from CH_2Cl_2/*n*-hexane a blue solid was obtained. Yield: 285 mg (324 µmol, 51%).

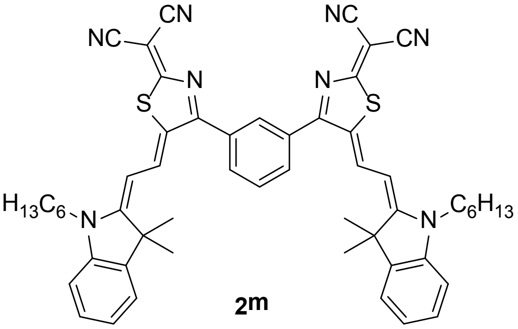


2p

Mp.: > 350 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.08 (d, J = 13.9 Hz, 2H), 7.95 (s, 4H), 7.45–7.37 (m, 4H), 7.29 (m, 2H), 7.15 (m, 2H), 5.95 (d, J = 13.9 Hz, 2H), 4.02 (t, J = 7.6 Hz, 4H), 1.91–1.86 (m, 4H), 1.59 (s, 12H), 1.50–1.34 (m, 12H), 0.92 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 179.9, 175.0, 172.3, 142.2, 141.3, 141.2, 136.0, 130.6, 129.2, 127.4, 126.4, 122.9, 118.6, 116.5, 111.5, 101.9, 50.1, 45.2, 31.8, 28.1, 27.8, 27.0, 22.9, 14.2. HRMS (ESI, positive, acetonitrile / chloroform): *m/z* 901.3804 $[M\text{+Na}]^+$, calculated for $C_{54}H_{54}N_8S_2Na$: 901.3805. UV-Vis (CH_2Cl_2): λ_{max} (ε) = 644 nm (179000 L mol^{-1} cm^{-1}). Elemental analysis (%): found: C, 73.81; H, 6.28; N, 12.80; S, 7.13; calculated for $C_{54}H_{54}N_8S_2$: C, 73.77; H, 6.19; N, 12.75; S, 7.29.

1,3-Phenylene-bis(merocyanine) **2m**:

A solution of **4b** (600 mg, 1.61 mmol; 1 equiv.) and **8** (961 mg, 3.54 mmol; 2.2 equiv.) in 2 mL acetic anhydride was heated to 90 °C for 30 min. After cooling down to room temperature, *iso*-propanol was added and the precipitate separated by filtration, washed with toluene and *n*-hexane and subsequently purified by column chromatography (CH_2Cl_2/MeOH 100 : 2 v/v). After recrystallization from CH_2Cl_2/*n*-hexane a blue solid was obtained. Yield: 380 mg (432 µmol, 30%).

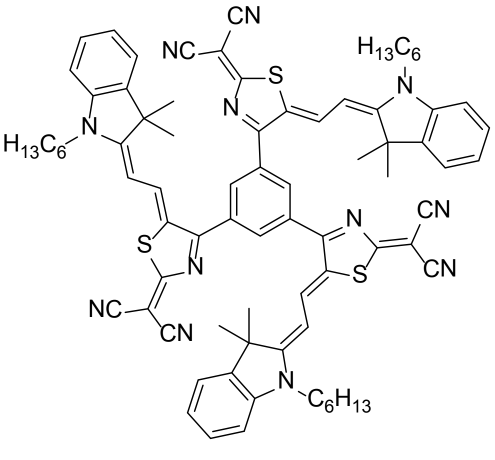


2m

Mp.: 295 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.04 (d, J = 13.9 Hz, 2H), 7.98 (m, 1H), 7.94–7.90 (m, 2H), 7.79 (m, 1H), 7.49 (m, 2H), 7.41 (m, 2H), 7.30 (m, 2H), 7.15 (m, 2H), 5.92 (d, J = 13.9 Hz, 2H), 4.02 (t, J = 7.5 Hz, 4H), 1.88–1.78 (m, 4H), 1.60 (s, 12H), 1.49–1.28 (m, 12H), 0.91 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 180.0, 175.6, 172.4, 142.1, 141.64, 141.57, 134.7, 132.3, 129.9, 129.8, 129.1, 127.1, 126.6, 123.3, 118.8, 116.9, 111.4, 101.8, 50.4, 45.3, 31.8, 28.2, 27.8, 27.0, 22.9, 14.2 HRMS (ESI, positive, acetonitrile/chloroform): *m/z* 878.3910 $[M]^+$, calculated for $C_{54}H_{54}N_8S_2$: 878.3907. UV-Vis (CH_2Cl_2): λ_{max} (ε) = 626 nm (178000 L mol^{-1} cm^{-1}). Elemental analysis (%) found: C, 73.41; H, 6.31; N, 12.53; S, 7.23; calculated for $C_{54}H_{54}N_8S_2$: C, 73.77; H, 6.19; N, 12.75; S, 7.29.

1,3,5-Phenylene-tris(merocyanine) **3**:

A solution of **4c** (500 mg, 962 µmol; 1 equiv.) and **8** (784 mg, 2.89 mmol; 3 equiv.) in 2 mL acetic anhydride was heated to 90 °C for 30 min. After cooling down to room temperature, *iso*-propanol was added and the precipitate separated by filtration, washed with toluene and *n*-hexane and subsequently purified by column chromatography (CH_2Cl_2/MeOH 100 : 1 v/v). After recrystallization from CH_2Cl_2/*n*-hexane a blue solid was obtained. Yield: 124 mg (96.9 µmol, 10%).



3

Mp.: > 380 °C (decomposition). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.35 (s, 3H) 8.19 (d, J = 14.0 Hz, 3H), 7.51 (m, 3H), 7.43 (m, 3H), 7.33 (m, 3H), 7.18 (m, 3H), 6.00 (d, J = 14.0 Hz, 3H), 4.06 (t, J = 7.6 Hz, 6H), 1.90–1.80 (m, 6H), 1.63 (s, 18H), 1.48–1.31 (m, 18H), 0.91 (t, J = 7.1 Hz, 9H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 179.6, 176.2, 170.1, 142.0, 141.9, 141.4, 135.4, 132.5, 129.2, 127.0, 126.9, 123.4, 119.0, 117.0, 111.7, 102.6, 50.7, 45.5, 31.8, 30.1, 28.2, 27.0, 22.9, 14.2. HRMS (ESI, positive mode, acetonitrile/chloroform): *m/z* found 1278.5625 $[M]^+$, calculated for $C_{78}H_{78}N_{12}S_3$: 1278.5629. UV-Vis (CH_2Cl_2): λ_{max} (ε) = 623 nm (209000 L mol^{-1} cm^{-1}). Elemental analysis (%) found: C, 73.03; H, 6.27; N, 12.64; S, 7.17; calculated for $C_{78}H_{78}N_{12}S_3$: C, 73.21; H, 6.14; N, 13.13; S, 7.52.

3. NMR spectra

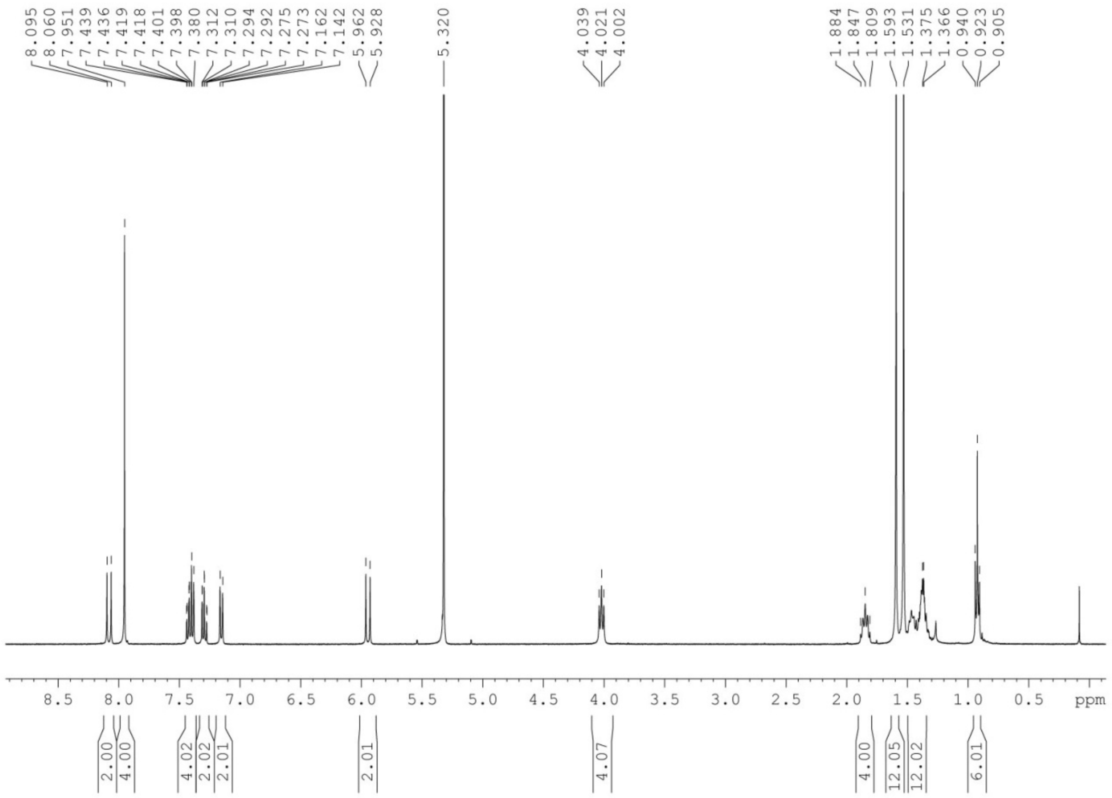


Fig. S1 ^{1}H NMR (400 MHz) spectrum of **2p** in CD_2Cl_2 at 295 K.

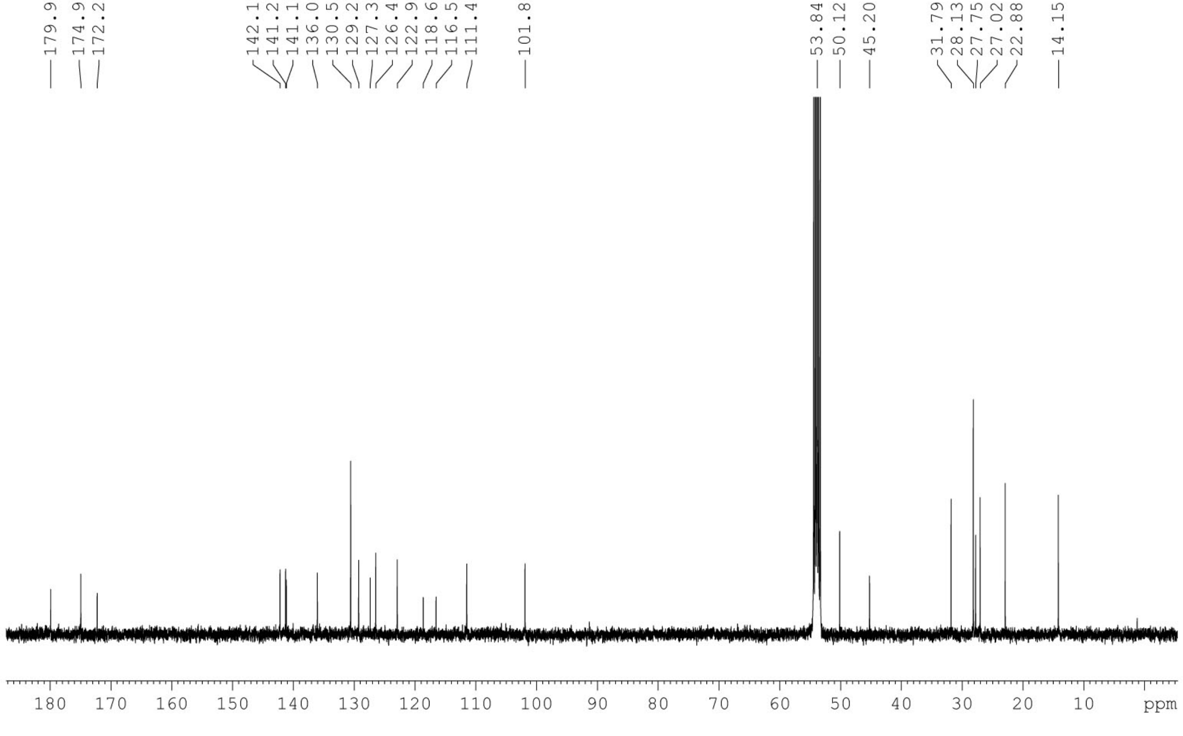


Fig. S2 ^{13}C NMR (101 MHz) spectrum of **2p** in CD_2Cl_2 at 295 K.

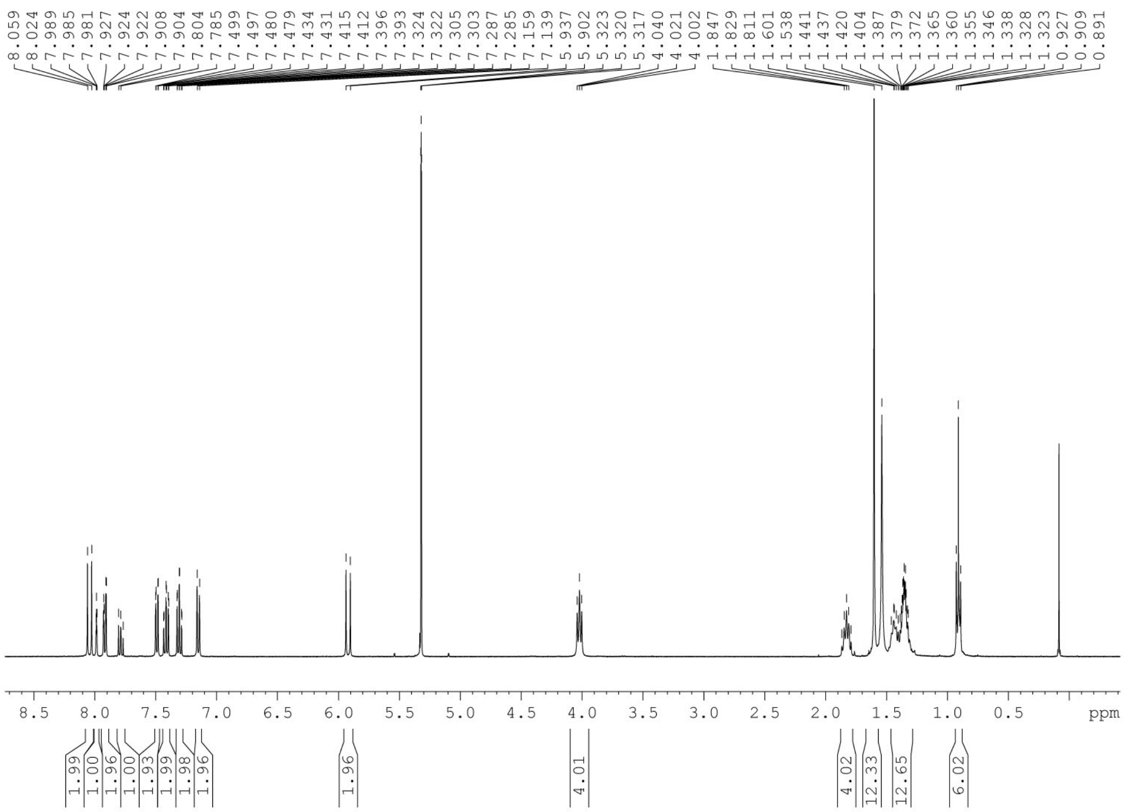


Fig. S3 ^{1}H NMR (400 MHz) spectrum of **2m** in CD_2Cl_2 at 295 K.

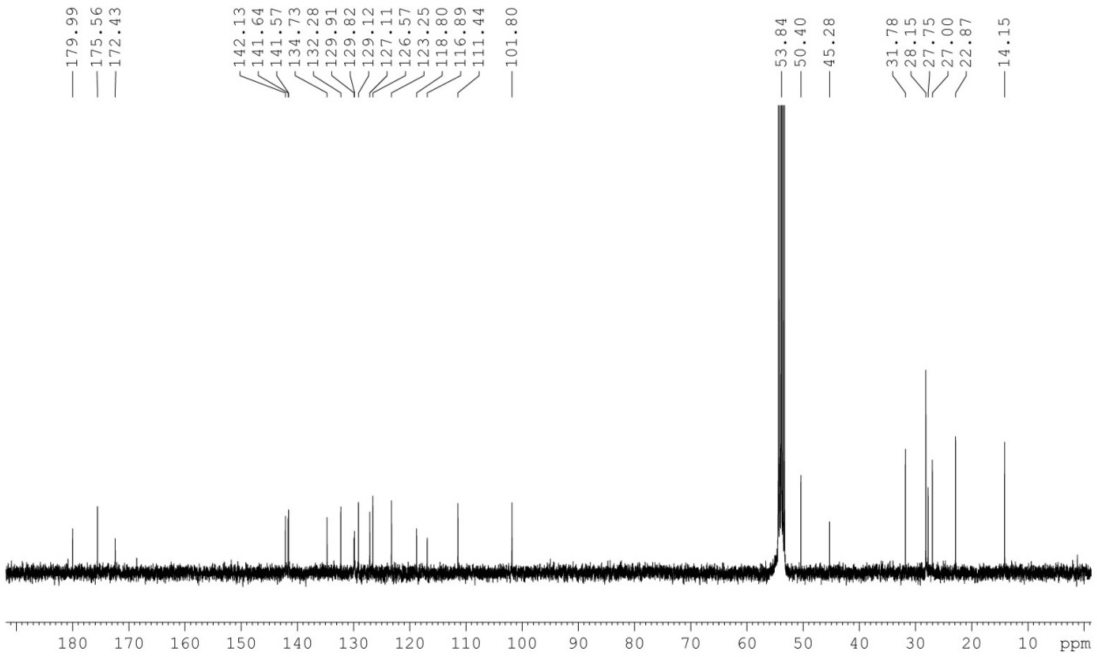


Fig. S4 ^{13}C NMR (101 MHz) spectrum of **2m** in CD_2Cl_2 at 295 K.

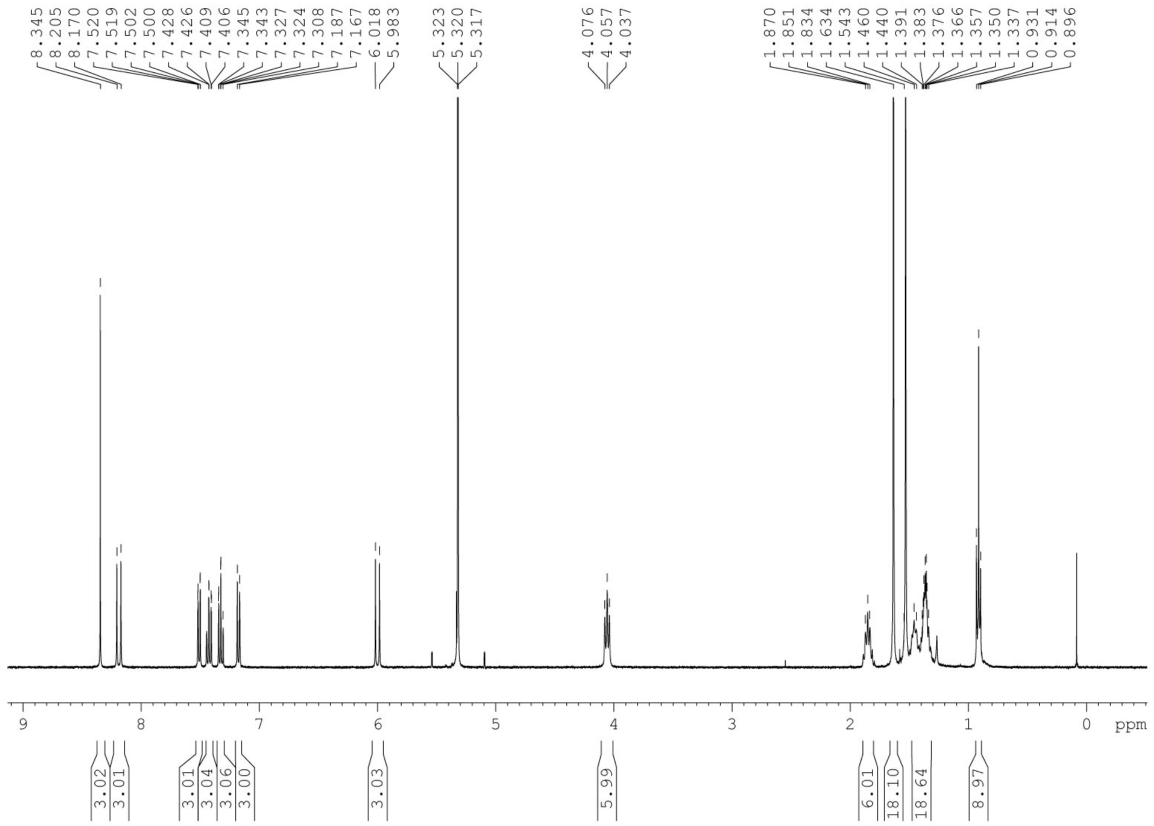


Fig. S5 ^{1}H NMR (400 MHz) spectrum of **3** in CD_2Cl_2 at 295 K.

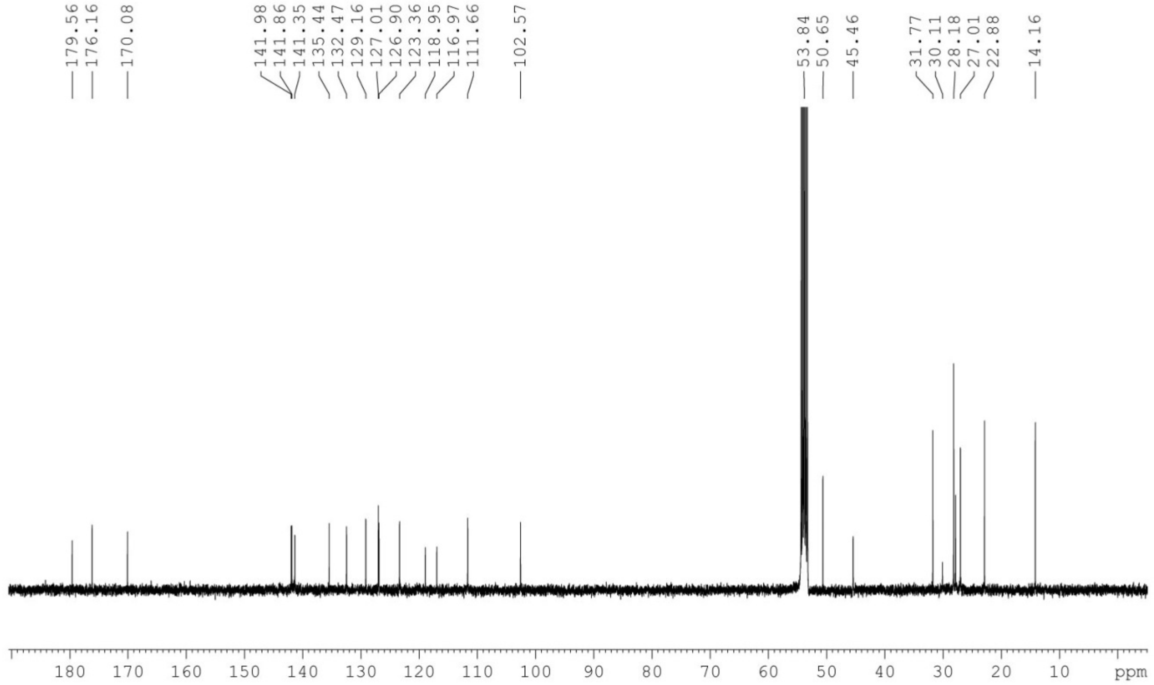


Fig. S6 ^{13}C NMR (101 MHz) spectrum of **3** in CD_2Cl_2 at 295 K.

4. DFT calculations

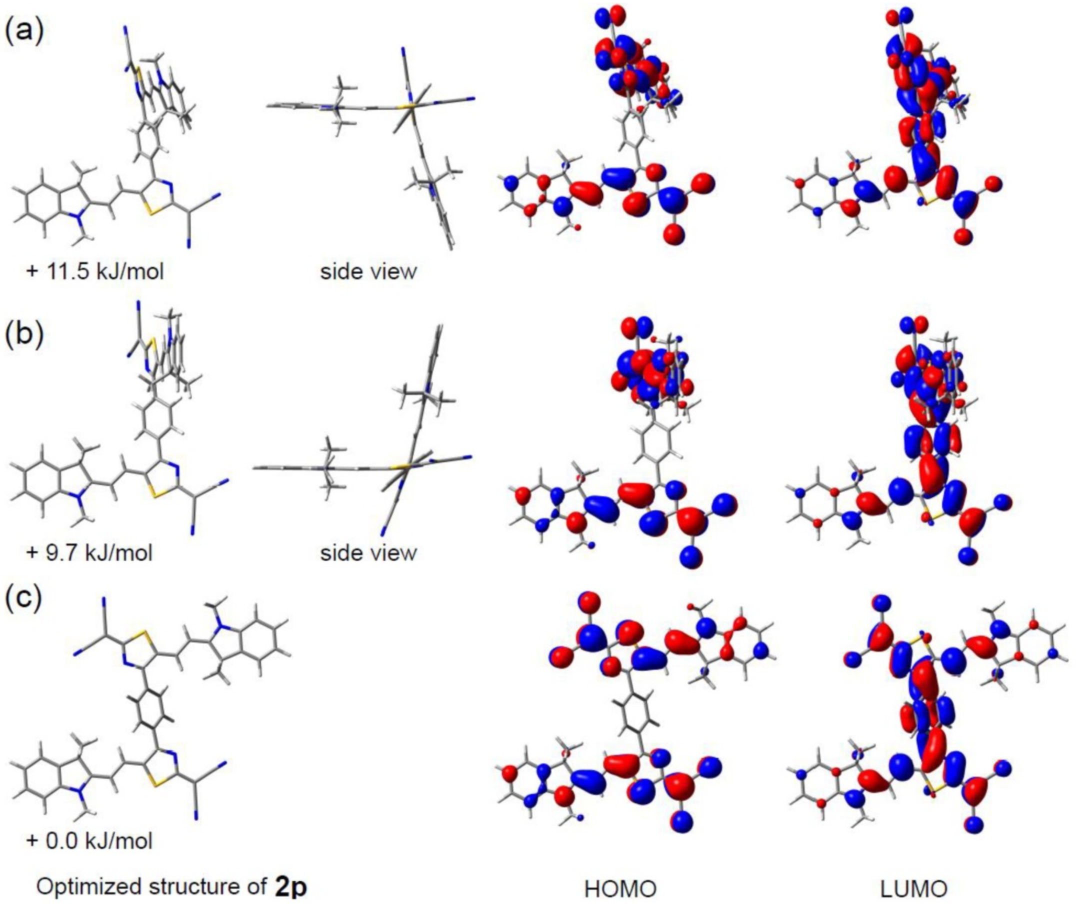


Fig. S7 Optimized structures (B3LYP/def2-SVP level) of **2p** based on different parallel (a) and antiparallel (b, c) starting geometries of the individual chromophores. Relative energies in comparison to the energetically most stable structure are given below the optimized geometries. Additionally, resulting electron densities of the HOMO and LUMO corresponding to the optimized structures are given.

Fig. S7 and Fig. S8 depict the optimized structures (B3LYP/def2-SVP level) for **2p** and **2m**, respectively. Different chromophore orientations (parallel and antiparallel) were chosen as starting geometries to avoid the optimization of local minima. For both dimers (**2p** and **2m**) the energetically most stable structure is an antiparallel orientation of the chromophores as depicted in Fig. 3 (main text), which is in agreement with the strongly reduced ground-state dipole moments observed in the electro-optical absorption measurements (cf. Sec IIA). Additionally, the HOMO−1 and LUMO+1 (Fig. S8c) for the optimized antiparallel structure of **2m** indicate that both chromophores of **2m** are not energetically degenerate as it is the case for **2p**.

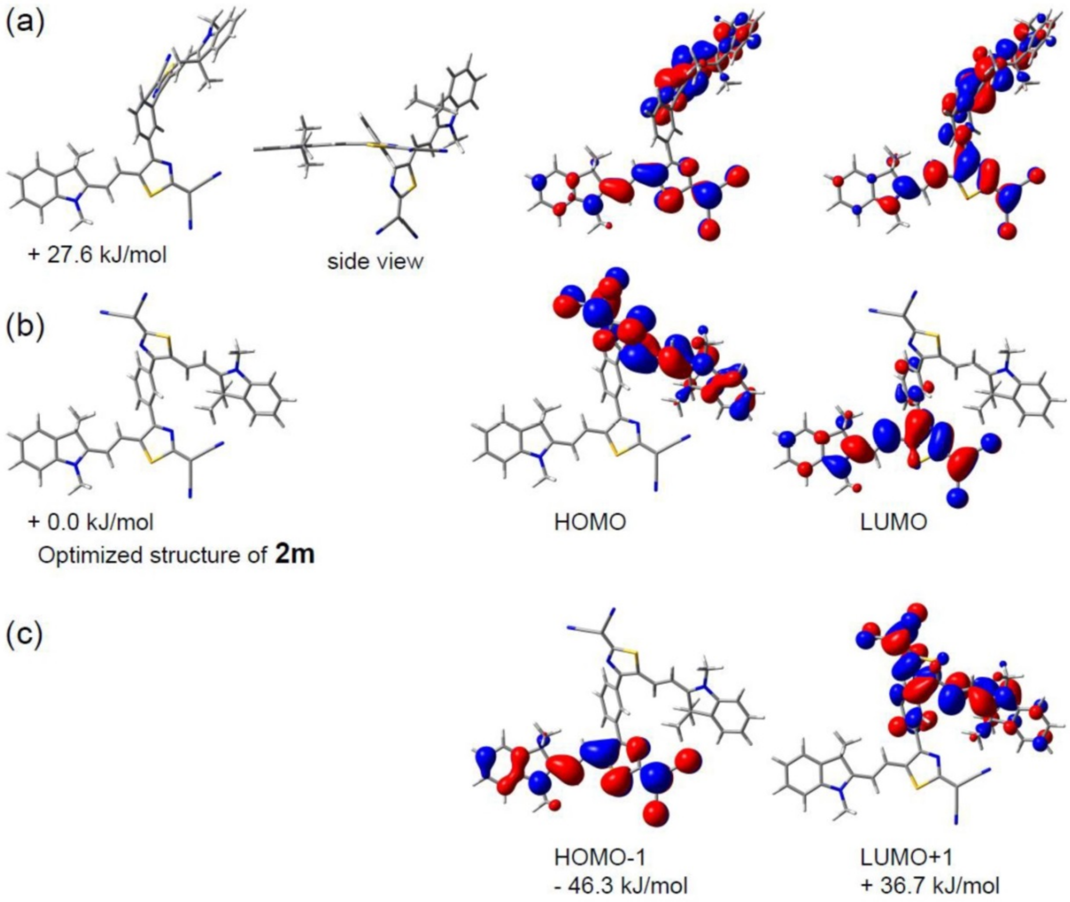


Fig. S8 Optimized structures (B3LYP/def2-SVP level) of **2m** based on a parallel (a) and antiparallel (b) starting geometry of the individual chromophores. Relative energies in comparison to the energetically most stable structure are given below the optimized geometries. Additionally, resulting electron densities of the HOMO and LUMO corresponding to the optimized structures are given. (c) HOMO−1 and LUMO+1 for the antiparallel structure depicted in (b).

5. Calculation of the exciton coupling energy V

The exciton coupling energy V based on the structure optimization in DFT was calculated by

$$V = \frac{1}{4\pi\varepsilon_0}\frac{|\mu_A||\mu_B|}{R^3}\left[\cos(\theta_{AB}) - 3\cos(\theta_A)\cos(\theta_B)\right], \tag{S1}$$

where ε_0 corresponds to the dielectric constant in vacuum, while μ_A and μ_B correspond to the two interacting transition dipole moments which are separated by the distance R. The angles θ_A and θ_B refer to the angles enclosed by the respective transition dipole moment with the connection axis of the point dipoles, and θ_{AB} refers to the angle between both transition dipole moments. In Table S1, the corresponding values derived from the geometry optimization of the DFT calculations (cf. subsection Density Functional Theory in the main article) are presented.

Table S1 Overview of the determined angles and distances between two chromophores for **2p** and **2m** based on the structural optimization by DFT. Additionally, the exciton coupling energies, which are determined by exciton theory V_{DFT} and determined by the fit of Gaussian functions to the linear absorption spectra V_{fit} (cf. Fig. 5 and Table S2), are given. For the calculation we used $\mu_A=\mu_B=\mu_{eg}=34.8\text{x}10^{-30}$ Cm, i.e., the value determined in our EOA experiment for **1**.

Dye	θ_A / °	θ_B / °	θ_{AB} / °	R / Å	V_{DFT} / cm^{-1}	V_{fit} / cm^{-1}
2p	119.50	119.55	0.00	8.39	249	700
2m	105.70	131.53	18.60	7.33	568	647

In order to calculate the dependence of V for the bis-chromophoric systems (**2p** and **2m**) on the relative chromophore orientation, we calculated V in dependence of the tilting angle φ and the rotation angle γ. While γ denotes the rotation angle around the connecting bond between the benzene spacer and the merocyanine moiety, φ denotes the tilting angle enclosed by the connecting bond and the vector of the dipole moment (cf. molecular structures and angles in Fig. 6 of the main article). For every set of φ and γ the angles θ_{AB}, θ_A, θ_B, and the distance R were determined to calculated V by Eq. S1.

6. Fit of the linear absorption spectra

Figure S9 depicts the fit (dashed, purple) of the linear absorption spectrum of **1** (solid red) by four Gaussians (dashed, black). The spectral shape of the absorption spectrum of **1** can be explained by a vibrational progression of the $S_0 \rightarrow S_1$ transition. Hence, we fitted the spectrum with four Gaussians (Fig. S9) which were restricted to have the same spectral width. The amplitudes (A_i) and central positions x_i of the different Gaussians (i) were free parameters. The retrieved results of the fitting routine are collected in Table S2. The results show a similar separation of $\approx 1000\ \mathrm{cm}^{-1}$ of the four Gaussians, as expected in the case of a vibronic progression.

For the dimers (**2m** and **2p**) six Gaussians were chosen to fit the linear absorption spectra (see Fig. 5). All six Gaussians were restricted to the spectral width obtained by the fit of the linear absorption spectrum of **1**, while four of the six Gaussians were additionally fixed at the spectral positions of the fit of **1**. Thus, the amplitudes of all six Gaussians were fitted as free parameters, while the two additional Gaussians for **2p** and **2m** compared to **1** were required to determine the excitonic splitting (V) due to the interaction of the two merocyanine chromophores. The fitting results are presented in Table S2.

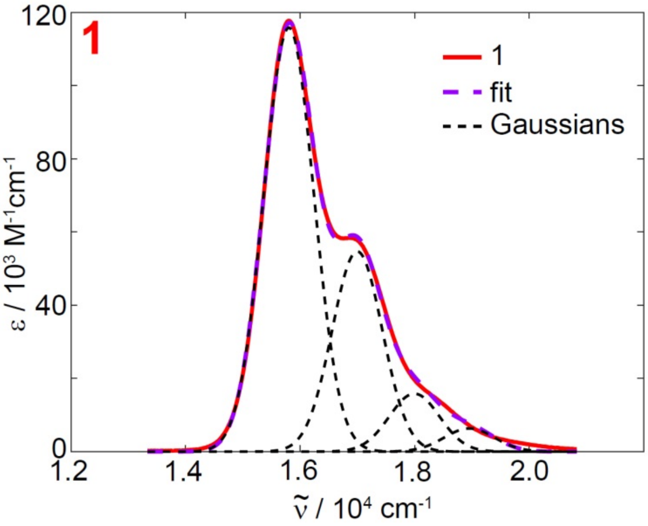


Fig. S9 Linear absorption of **1** (red), fitted by four Gaussian with identical widths, and fit result (purple, dashed). Details of the fitting routine are given in the text.

Table S2 Overview of the fitting results of the linear absorption spectra of **1** (cf. Fig. S9), **2p**, and **2m** (cf. Fig. 5). For **1**, the width of all Gaussians was forced to be identical, with free central positions (x_i) and amplitudes (A_i). For **2p** and **2m**, x_i and the width of **1** were used, while the amplitudes were fitted as free parameters. Additionally, two Gaussian functions (i = 5, 6) were chosen to fit the excitonic bands for the dimers, denoted with A_i^{exc} and x_i^{exc}.

Dye	**1**	**2p**	**2m**
width / cm^{-1}	439	439	439
A_1 / 10^4 cm^{-1}	11.5	10.9	14.7
x_1 / 10^4 cm^{-1}	1.58	1.58	1.58
A_2 / 10^4 cm^{-1}	5.47	4.91	10.0
x_2 / 10^4 cm^{-1}	1.70	1.70	1.70
A_3 / 10^4 cm^{-1}	1.58	2.34	3.37
x_3 / 10^4 cm^{-1}	1.80	1.80	1.80
A_4 / 10^4 cm^{-1}	0.63	1.46	1.07
x_4 / 10^4 cm^{-1}	1.90	1.90	1.90
A_5^{exc} / 10^4 cm^{-1}	-	11.1	1.51
x_5^{exc} / 10^4 cm^{-1}	-	1.52	1.51
A_6^{exc} / 10^4 cm^{-1}	-	4.31	4.36
x_6^{exc} / 10^4 cm^{-1}	-	1.66	1.64

7. References

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