Electronic Supporting Information

Enhanced photocurrent generation by folding-driven H-aggregate formation

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1 Experimental

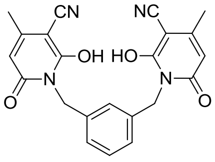
1.1 Materials and methods

All solvents and reagents were purchased from commercial sources and used as received without further purification, unless otherwise stated. The starting compound **1** was prepared according to literature procedure.[S1] Column chromatography was performed using silica gel 60M (0.04–0.063 mm) from Macherey-Nagel. Melting points were determined on an Olympus BX41 polarization microscope and are uncorrected. ^{1}H NMR spectra were recorded on Bruker Advance 400 or Bruker Advance DMX 600 and calibrated to the residual solvent peak. All chemical shifts are in ppm. High-resolution mass spectra (ESI) were recorded on an ESI MicrOTOF Focus spectrometer from Bruker Daltonics. Elemental analyses were performed on a CHNS 932 analyzer (Leco Instruments GmbH, Mönchengladbach, Germany). For all spectroscopic measurements, spectroscopic grade solvents (Uvasol) from Merck (Hohenbrunn, Germany) were used. UV/vis spectra of the synthesized compounds were recorded on a Perkin Elmer UV/vis spectrometer Lamda 950, Perkin Elmer UV/vis spectrometer Lamda 35 and Perkin Elmer UV/vis spectrometer Lamda 40P.

1.2 Synthesis

1.2.1 Synthesis of the bis(pyridone) precursor 2

To a suspension of 12.1 g (44.8 mmol) of the diamide **1** in 20 mL piperidine was added 35.0 g (269 mmol) ethyl acetoacetate and the resulting mixture was heated at 100 °C for 2.5 h. After being cooled to room temperature, the pH value was adjusted to 1 with 32% aqueous HCl. The precipitated product **2** was separated by filtration, washed with plenty of water and dried in vacuo.



2

Yield: 13.9 g (34.5 mmol, 77%), colorless solid.

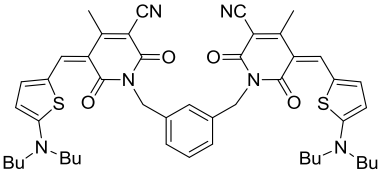
mp.: >300 °C, decomposition.

^{1}H NMR (400 MHz, d$_6$-DMSO): δ = 7.23 (t, ^3J = 7.7 Hz, 1H), 7.09 (t, ^4J = 1.4 Hz, 1H), 7.05 (dd, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 2H), 5.57 (s, 2H), 5.05 (s, 4H), 2.21 (s, 6H).

HRMS (EI): *m/z* 402.13190 [M]$^+$ (calcd. for $C_{22}H_{18}N_4O_4^+$ 402.13226).

1.2.2 Synthesis of the bis(merocyanine) dye 4

A mixture of 200 mg (0.50 mmol) bis(pyridone) **2** and of 262 mg (1.09 mmol) 5-(dibutylamino)-thiophene-2-carbaldehyde **3** in 2 mL Ac_2O was stirred at 90 °C for 30 min. The reaction mixture was treated with MeOH and *i*-PrOH. The solvent was evaporated and the residue was subjected to column chromatography (silica, CH_2Cl_2/MeOH 100/1.5). Subsequent precipitation from dichloromethane/*n*-hexane afforded the pure product.



4

Yield: 259 mg (0.31 mmol, 61%), red solid.

mp.: 283 °C.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.53 (s, 2H), 7.52 (d, ^3J = 5.3 Hz, 2H), 7.32 (s, 1H), 7.20–7.17 (m, 3H), 6.41 (d, ^3J = 5.3 Hz, 2H), 5.13 (s, 4H), 3.54 (t, ^3J = 7.6 Hz, 8H), 2.42 (s, 6H), 1.77–1.68 (m, 8H), 1.46–1.36 (m, 8H), 0.98 (t, ^3J = 7.4 Hz, 12H).

^{13}C NMR (151 MHz, CD_2Cl_2): δ = 176.61, 163.62, 162.50, 158.63, 152.65, 142.18, 138.20, 128.44, 127.15, 126.35, 124.89, 117.77, 111.39, 107.03, 94.55, 54.33, 42.90, 29.61, 20.41, 19.02, 13.94.

HRMS (ESI, pos. mode, acetonitrile/chloroform): *m/z* 844.37989 [M]$^+$ (calcd. for $C_{48}H_{56}N_6O_4S_2^+$ 844.37990).

UV/vis (CH_2Cl_2, $c = 4.9\times10^{-6}$ M): λ_{max} / nm (ε_{max} / L mol^{-1} cm^{-1}) = 539 (255600).

CHN analysis (%): calculated for $C_{48}H_{56}N_6O_4S_2$: C, 68.22; H, 6.68; N, 9.94; S, 7.59; found: C, 68.04; H, 6.64; N, 9.98; S, 7.78.

2 UV/vis absorption spectra

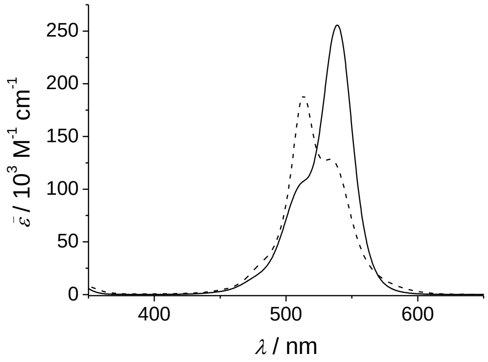


Fig. S1 UV/vis absorption spectra of bis(merocyanine) dye **4** in dichloromethane (solid line, $c = 4.9\times10^{-6}$ M) and in dioxane (dashed line, $c = 1.2\times10^{-5}$ M) at 25 °C.

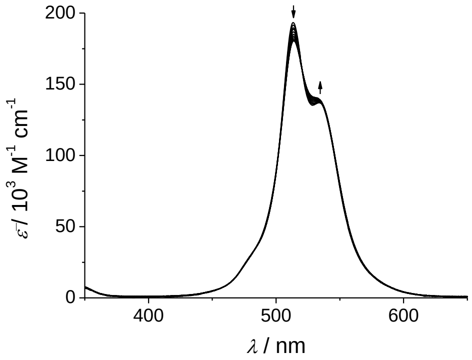
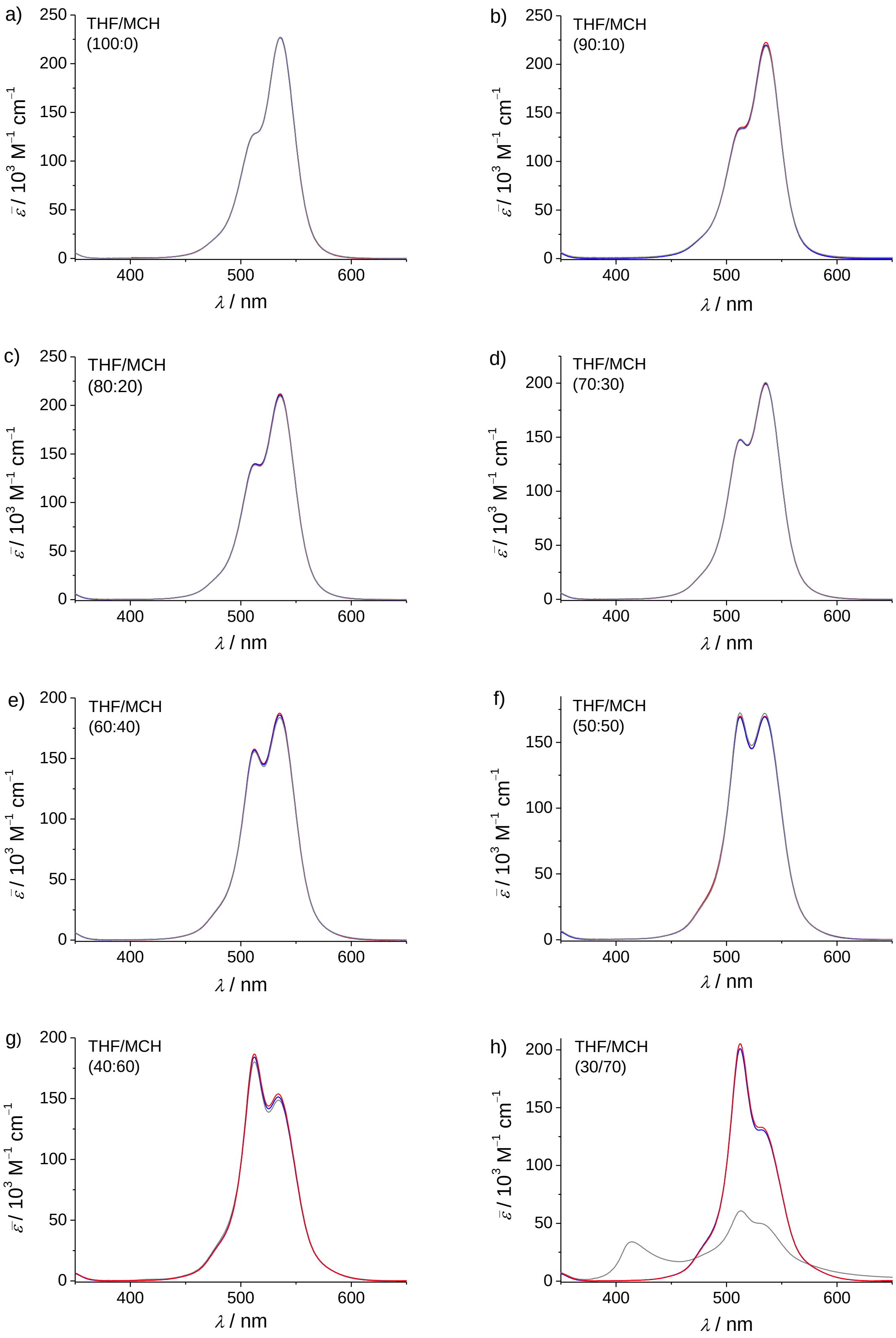


Fig. S2 Temperature-dependent UV/vis absorption spectra of bis(merocyanine) dye **4** in dioxane ($c = 1.5\times10^{-6}$ M). Arrows indicate the spectral changes upon increasing the temperature from 20 to 70 °C.


a)
THF/MCH
(100:0)
b)
THF/MCH
(90:10)
c)
THF/MCH
(80:20)
d)
THF/MCH
(70:30)
e)
THF/MCH
(60:40)
f)
THF/MCH
(50:50)
g)
THF/MCH
(40:60)
h)
THF/MCH
(30/70)
$\bar{\varepsilon}$ / 10^3 M^{-1} cm^{-1}
λ / nm
0
50
100
150
200
250
400
500
600

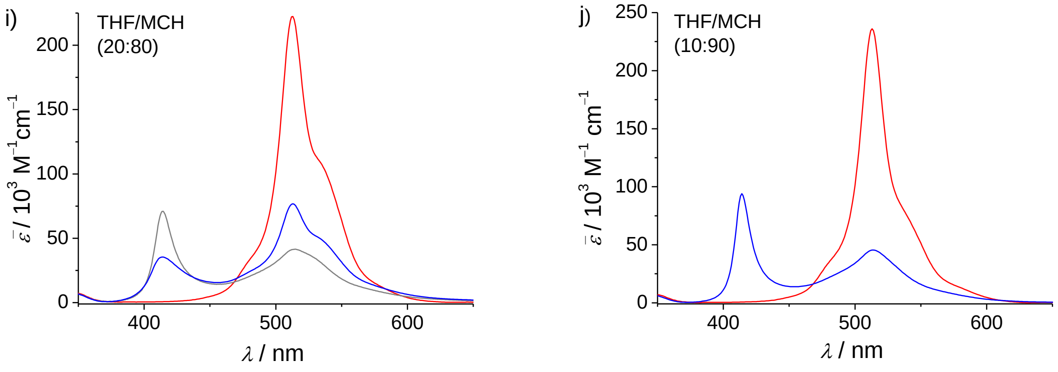


Fig. S3 UV/vis spectra of bis(merocyanine) dye **4** in THF/MCH mixtures at different concentrations of $c = 1\times10^{-6}$ M (red line), $c = 5\times10^{-6}$ M (blue line) and $c = 2\times10^{-5}$ M (grey line) and varying solvent composition: (a) 100% THF; (b) 90% THF; (c) 80% THF; (d) 70% THF; (e) 60% THF; (f) 50% THF; (g) 40% THF; (h) 30% THF; (i) 20% THF; (j) 10% THF (grey line is missing due to precipitation at $c = 2\times10^{-5}$ M).

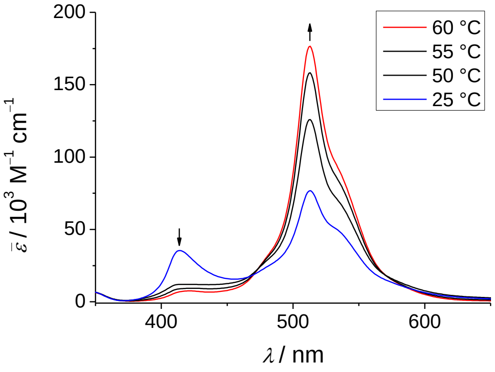


Fig. S4 Temperature-dependent UV/vis spectra of dye **4** in a THF/MCH = 20:80 mixture ($c = 5\times10^{-6}$ M).

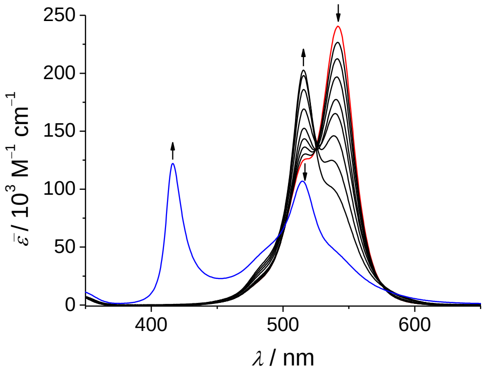
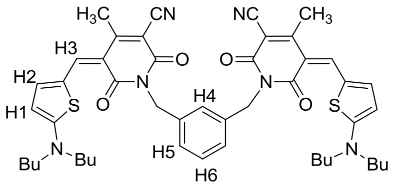


Fig. S5 Solvent-dependent UV/vis spectra of dye **4** in $CHCl_3$/MCH mixtures ($c = 1\times10^{-5}$ M) at 25 °C starting in pure $CHCl_3$ (red line) and increasing the volume fraction of MCH in 10% steps. Arrows indicate the spectral changes upon increasing the volume fraction of MCH.

3 Structure elucidation by NMR spectroscopy



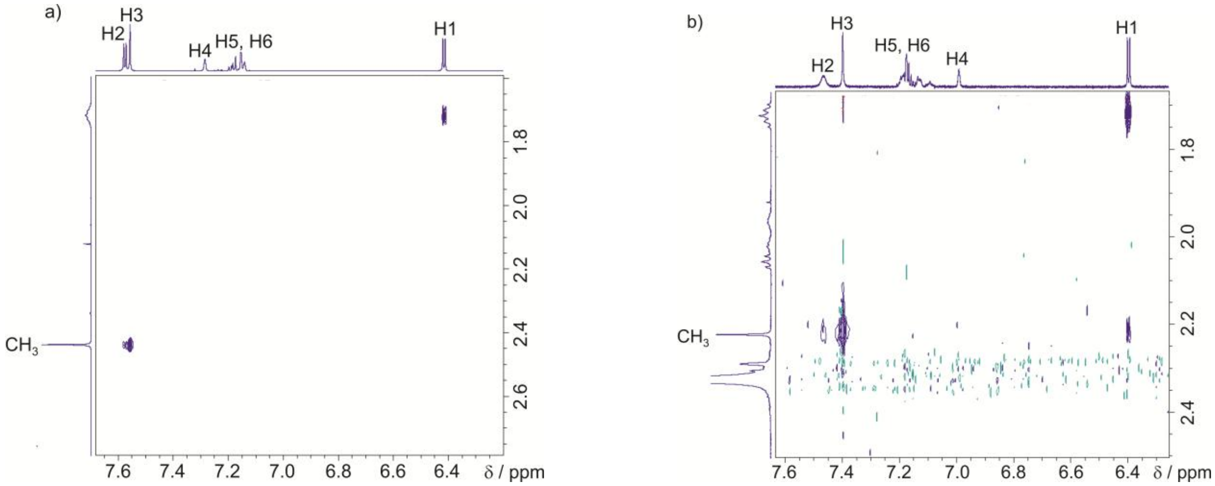


Fig. S6 Selected areas of the 600 MHz ROESY NMR spectra of bis(merocyanine) dye **4** in (a) dichloromethane ($c = 1.0{\times}10^{-3}$ M, $T = 25$ °C) and (b) dioxane ($c = 2.5{\times}10^{-4}$ M, $T = 50$ °C).

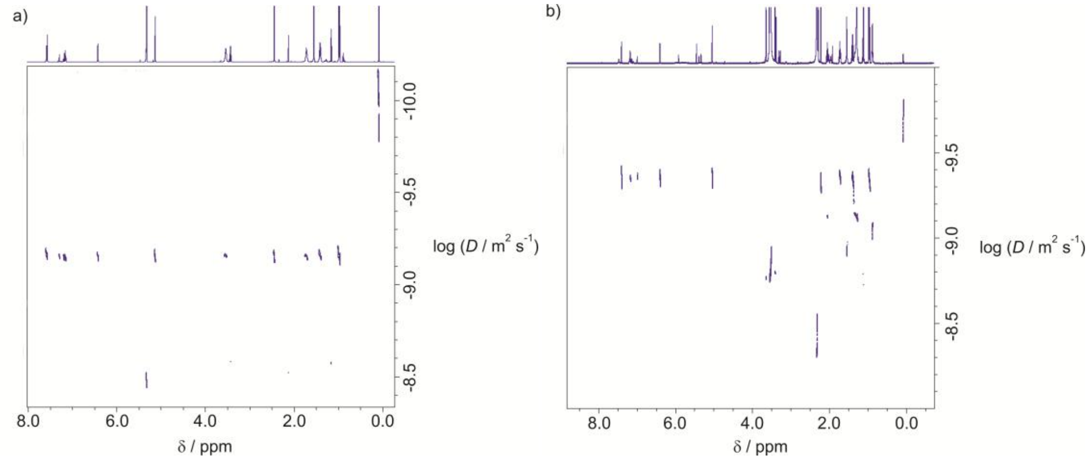


Fig. S7 600 MHz DOSY NMR spectra of bis(merocyanine) dye **4** in (a) CD_2Cl_2 ($c = 1.0{\times}10^{-3}$ M, $T = 25$ °C) and in (b) dioxane-d_8 ($c = 2.5{\times}10^{-4}$ M, $T = 50$ °C). The diffusion coefficients D (in $m^2\ s^{-1}$) are plotted on a logarithmic scale against the chemical shift δ.

To estimate the size of bis(merocyanine) dye **4** in solution, the Stokes-Einstein equation (S1) for spherical particles has been applied

$$D = \frac{k_B T}{6\pi\eta r} \tag{S1}$$

where D is the diffusion coefficient of the compound, k_B the Boltzmann constant, T the temperature, η the viscosity of the solvent, and r the hydrodynamic radius of the molecule.

In dichloromethane a diffusion coefficient of $D = 6.98\times10^{-10}$ m^2/s was determined, whereas in dioxane a diffusion coefficient of $D = 4.40\times10^{-10}$ m^2/s was found for compound **4**.

With equation (S1) using tabulated values for solvent viscosities a hydrodynamic radius of the molecules of $r = 7.59$ Å in dichloromethane and $r = 6.83$ Å in dioxane were calculated. These values exclude the formation of oligomeric species in solution and corroborate the view of a smaller hydrodynamic radius for the folded state.

4 K_{eq} and ΔG values for folding

For the thermodynamic analysis of the folding process a literature known procedure established by Moore was applied. The details for the derivation of the applied equations are given in literature.[S2] For the preceding two-state equilibrium of bis(merocyanine) dye **4** (S2)

$$\text{unfolded} \xrightleftharpoons{K_{eq},\ \Delta G} \text{folded} \tag{S2}$$

the quantitative thermodynamic values can be determined as follows: With the assumption that the absorbance values A_F obtained in the THF/MCH = 10:90 mixture and A_U obtained in pure THF coincide with the ideal spectra of the folded and unfolded dye **4**, the mole fraction of **4** in the unfolded state $\alpha_{unfolded}$ can be calculated for all solvent compositions according to equation (S3).

$$\alpha_{unfolded} = \frac{A_F - A}{A_F - A_U} \tag{S3}$$

The equilibrium constant K_{eq} and related Gibbs free energy changes ΔG for the conformational switch between unfolded and folded state can be calculated by using equations (S4) and (S5).

$$K_{eq} = \frac{\alpha_{folded}}{\alpha_{unfolded}} = \frac{1 - \alpha_{unfolded}}{\alpha_{unfolded}} \tag{S4}$$

$$\Delta G = -RT \ln K_{eq} \tag{S5}$$

The free energy change between both conformational states is assumed to linearly depend on solvent composition in analogy to the solvent denaturation of proteins and peptide secondary structures.[S3] This allows to obtain the extrapolated free energy change in pure MCH by linear regression analysis of the experimental data points according to equation (S6).

$$\Delta G = \Delta G(MCH) - m[THF] \tag{S6}$$

Table S1 Thermodynamic data derived for the solvent-dependent folding of bis(merocyanine) dye **4**.

Vol% THF in MCH	K_{eq} (536 nm)	K_{eq} (513 nm)	ΔG (536 nm) / kJ mol^{-1}	ΔG (513 nm) / kJ mol^{-1}
0	-	-	-	-
10	-	-	-	-
20	5.25	6.69	–4.1	–4.7
30	2.08	2.41	–1.8	–2.2
40	1.06	1.16	–0.1	–0.4
50	0.64	0.66	1.1	1.0
60	0.37	0.38	2.4	2.4
70	0.22	0.23	3.7	3.6
80	0.11	0.14	5.6	4.9
90	0.02	0.08	9.2	6.3
100	-	-	-	-

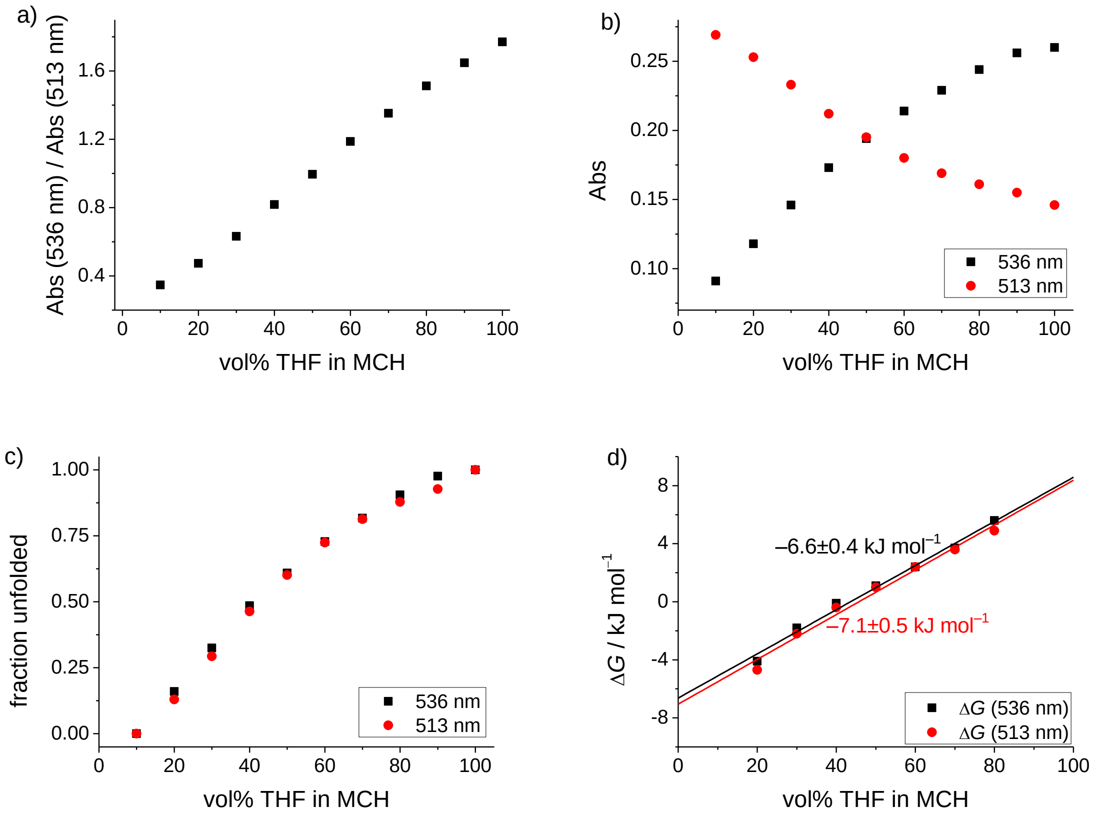


Fig. S8 (a) Plot of the intensity ratios of the absorbance at 536 and 513 nm versus solvent composition. (b) Plot of the absorbance of **4** at 536 nm (■) and 513 nm (●) against the vol% of THF in MCH. (c) Plot of $\alpha_{unfolded}$ of **4** at 536 nm and 513 nm against the vol% of THF in MCH. (d) Plot of the ΔG values for the folding process of **4** derived from the spectral development at 536 nm and 513 nm. The black and the red lines are the respective fitting results from linear regression analysis.

5 BHJ solar cells

5.1 Device fabrication and characterization

All devices were fabricated on commercial indium-tin oxide (ITO) coated glass. The ITO was etched with $FeCl_3$/HCl solution and subsequently cleaned using chloroform, acetone, mucasol detergent and de-ionized water in ultrasonic bath. As next, the ITO substrates were exposed to ozone for 20 minutes and immediately coated with poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios Al 4083, Heraeus; ca. 40 nm). Afterwards, the samples were heat treated for 2 minutes at 110 °C to remove residual water and transferred into a N_2 glove box for the fabrication of devices and measurements.

The dye and PCBM (≥99.5%, Nano-C) were separately dissolved (10 mg mL^{-1} each) in chloroform (≥99.8%, Sigma Aldrich). The solutions were mixed with specific volumes to give the desired donor:acceptor weight ratio. The secondary solvent (toluene, ≥99.9% Merck; *o*-xylene, >98% Fluka; chlorobenzene, 99.9% Sigma Aldrich; *o*-dichlorobenzene, >98% Fluka) was added to the blend solutions yielding a volume fraction of 20%. For more accurate comparison, the same volume of chloroform was added for devices processed without solvent additive. Film thickness was adjusted by regulating the rotation speed for spin-coating. The substrates were transferred to a high-vacuum chamber where the top electrodes were evaporated. Here, a 120 nm thick Al (99.9% Alfa Aesar) layer was deposited through a mask. On each substrate, seven solar cells with an active area of 0.0785 cm^2 are obtained.

The *JV*–characteristics of the solar cells were measured using a Keithley 2425 source measurement unit with simulated AM1.5 sun light provided by a filtered Xe lamp. The intensity of 100 mW cm^{-2} of the light was determined by using a calibrated inorganic solar cell from the Fraunhofer Institute for solar research (ISE) in Freiburg, Germany and a reference P3HT:PCBM cell measured by the same institute. No spectral mismatch factor was included in the calculation of the efficiency. The *EQE* measurements were performed using an Oriel QE/IPCE Measurement Kit. Thin film absorption spectra were taken with a Varian Cary 50 UV/vis spectrometer. The absorption of glass/ITO/PEDOT:PSS was used for baseline correction. Layer thicknesses were determined with a Dektak surface profiler (Veeco).

5.2 UV/vis and BHJ solar cell data

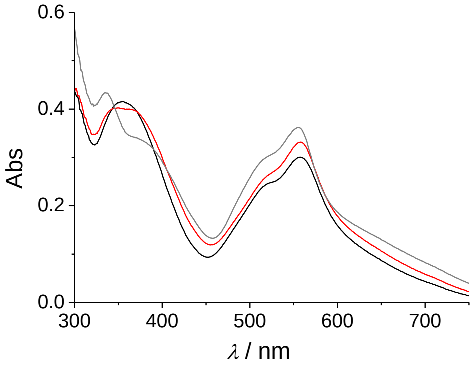


Fig. S9 Thin film absorption specta of **4**:PCBM (30:70) blends in dependence on the casting solvent mixture $CHCl_3$ (black line), $CHCl_3$/chlorobenzene (red line) and $CHCl_3$/*o*-dichlorobenzene (grey line).

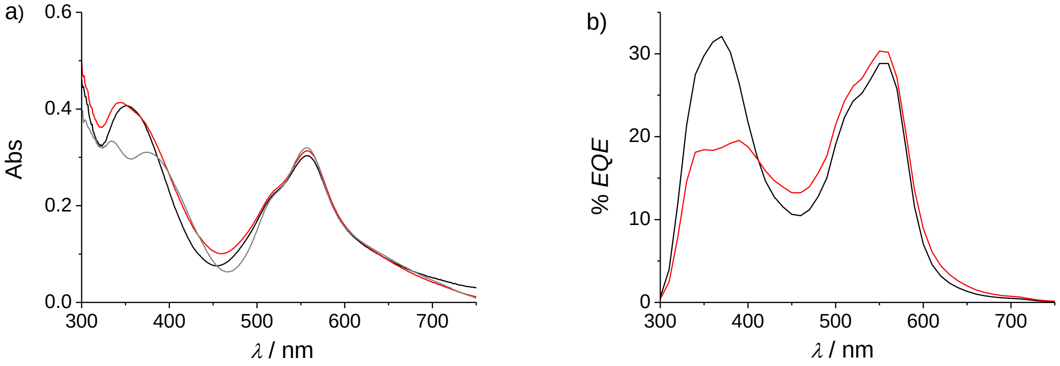


Fig. S10 (a) Thin film absorption and (b) *EQE* spectra of **5**:PCBM (30:70) blends in dependence on the casting solvent mixture $CHCl_3$ (black line), $CHCl_3$/toluene (red line) and $CHCl_3$/*o*-xylene (grey line).

Table S2 Device characteristics of **5**:PCBM (30:70) BHJ solar cells in dependence on the solvent mixture under AM1.5, 100 mW/cm^{-2} illumination.

solvent mixture (vol%)	V_{OC} /V	*FF*	J_{SC} /mA cm^{-2}	$J_{SC}(EQE)$ /mA cm^{-2}	% PCE
$CHCl_3$	0.83	0.34	2.58	2.72	0.73
$CHCl_3$/toluene (80:20)	0.78	0.34	2.72	2.87	0.73

The theoretical $J_{SC}(EQE)$ values were calculated by integration using equation (S7)

$$J_{SC}(EQE) = e\int EQE(\lambda) \cdot N_{ph}(\lambda) d\lambda \qquad \text{(S7)}$$

where e represents the elementary electric charge, $N_{ph}(\lambda)$ is the AM1.5 solar photon flux and $EQE(\lambda)$ is the measured external quantum efficiency.

The calculated $J_{SC}(EQE)$ values showed excellent agreement with the measured photocurrents in the solar cells (see Table S2).

6 ^{1}H NMR spectra

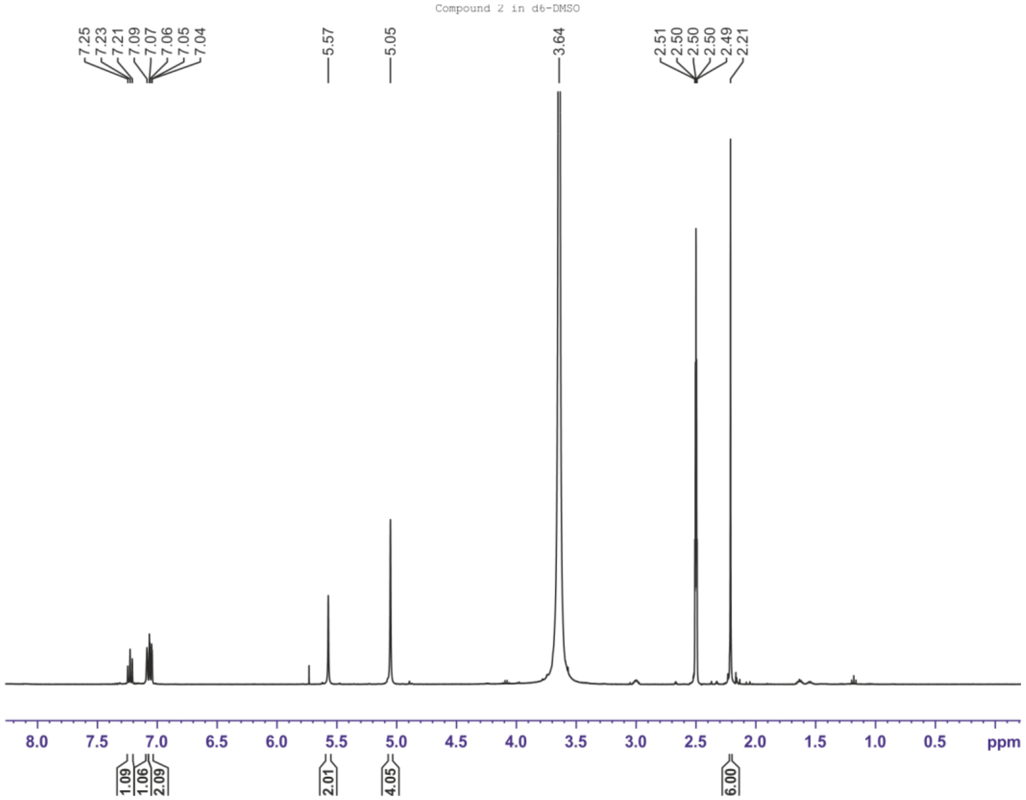


Fig. S11 ^{1}H NMR spectrum of compound **2** in d$_6$-DMSO.

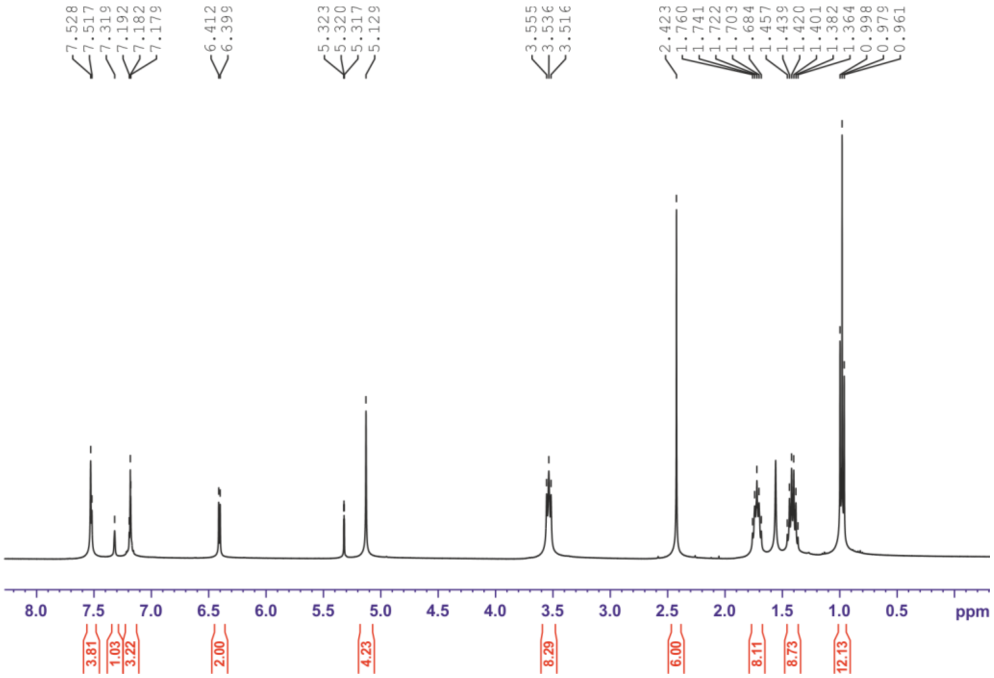


Fig. S12 ^{1}H NMR spectrum of compound **4** in CD_2Cl_2.

7 Additional references

S1. A. Gazit, N. Osherov, C. Gilon, A. Levitzki, *J. Med. Chem.* **1996**, *39*, 4905−4911.

S2. C. R. Ray, J. S. Moore, *Adv. Polym. Sci.* **2005**, *177*, 91−149.

S3. C. N. Pace, B. A. Shirley, J. A. Thompson, *Protein Structure: A Practical Approach*, *IRL Press, New York*, 1989.