Electronic Supplementary Information (ESI)

Cooperative self-assembly of squaraine dyes

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Table of Contents

1. Experimental

1.1 Materials and Methods

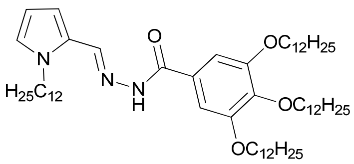
All solvents and reagents were purchased from commercial sources and used as received without further purification, unless otherwise stated. Compounds **1** and **2** were prepared according to literature procedures.[S1] Column chromatography was performed using silica gel Si60 (0.035–0.070 mm) from Acros Organics. For the isolation of the target squaraine **4**, preparative recycling GPC LC-9105, Japan Analytical Industry Co., Ltd. (JAI) with JAIGEL 2H+2.5H columns was used. 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 internal standard TMS or the residual solvent peak. All chemical shifts are in ppm. High-resolution mass spectra (ESI) were recorded on an ESI MicrOTOF Focus 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/NIR spectra of the synthesised compounds were recorded on a Perkin Elmer UV/vis/NIR spectrometer Lamda 950 and Perkin Elmer UV/vis/NIR spectrometer Lamda 35.

AFM measurements were performed under ambient conditions using a MultiMode Nanoscope IV system operating in tapping mode in air.

Dynamic light scattering experiments were performed on a Beckman Coulter N5 submicron Particle Size Analyzer using Helma fluorescence cuvettes and spectroscopic grade solvents (Uvasol®) from Merck (Hohenbrunn, Germany).

1.2 Synthesis of the donor unit 3



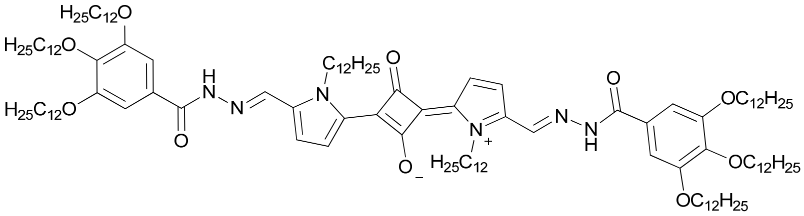
To a solution of 1.38 g (2.00 mmol) of **1** and 0.53 g (2.00 mmol) of *N*-dodecyl-pyrrol-2-aldehyde (**2**) in 20 mL ethanol were slowly added 0.136 g (2.00 mmol) of imidazole. The reaction mixture was heated to reflux for 5 h. The solvent was evaporated under reduced pressure and the residue was subjected to column chromatography over silica using CH_2Cl_2 as eluent. Compound **3** was isolated as a white solid.

$C_{60}H_{107}N_3O_4$ (934.51)

Yield: 953 mg (1.02 mmol, 55%); Mp.: 80 °C.

^{1}H NMR (400 MHz, CD_2Cl_2, TMS): δ = 8.70 (s, 1H, NH), 8.07 (s, 1H, CH), 6.93 (s, 2H, CH_{arom}), 6.74 (s, 1H, CH_{arom}), 6.43 (s, 1H, CH_{arom}), 6.07 (t, 1H, CH_{arom}), 4.23-4.19 (m, 2H, NCH_2), 3.94-3.90 (m, 6H, OCH_2), 1.75-1.62 (m, 8H, CH_2), 1.41-1.38 (m, 8H, CH_2), 1.29-1.18 (m, 64H, CH_2), 0.81-0.78 (m, 12H, CH_3). HRMS (ESI, positive, acetonitrile / chloroform): *m/z*: 934.83346 (M+H$^+$), calculated for $C_{60}H_{108}N_3O_4^+$: 934.83344.

1.3 Synthesis of target squaraine 4



In 4 mL of a 1:2 mixture of *n*-butanol/benzene, 49.6 mg (53.0 µmol) of compound **3** and 3.03 mg (27.0 µmol) of 3,4-dihydroxycyclobut-3-en-1,2-dione were heated to reflux for 4 h in the presence of molecular sieves (3 Å). The solvent was then removed under reduced pressure and the crude product was purified by repeated column chromatography over silica using different CH_2Cl_2/methanol mixtures (99.8-99.5:0.2-0.5%) as eluent, followed by GPC and subsequent precipitation from a CH_2Cl_2/methanol mixture.

$C_{124}H_{212}N_6O_{10}$ (1947.04)

Yield: 6.83 mg (3.51 µmol, 11%), blue solid; Mp.: 180 °C.

^{1}H NMR (400 MHz, d^8-THF, TMS): δ = 10.86 (s, 2H, NH), 8.63 (s, 2H, CH), 7.75 (d, ^3J(H,H) = 4.6, 2H, CH_{arom}), 7.11 (s, 4H, CH_{arom}), 6.82 (d, ^3J(H,H) = 4.6, 2H, CH_{arom}), 4.93 (m, 4H, NCH_2), 3.93-3.89 (t, ^3J(H,H) = 6.5, 12H, OCH_2), 1.72-1.69 (m, 16H, CH_2), 1.45-1.41 (m, 16H, CH_2), 1.29-1.17 (m, 128H, CH_2), 0.80-0.76 (m, 24H, CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 179.15, 168.28, 161.25, 153.41, 141.31, 131.74, 131.33, 128.40, 128.02, 124.57, 109.51, 105.59, 73.63, 69.48, 69.44, 64.23, 49.25, 32.25, 32.22, 31.65, 30.66, 30.07, 30.05, 30.03, 30.01, 29.98, 29.97, 29.92, 29.93, 29.92, 29.86, 29.82, 29.76, 29.71, 29.69, 29.64, 29.50, 28.84, 26.77, 26.43, 26.11, 23.14, 22.98, 22.80, 14.34, 14.17, 13.99. HRMS (ESI, positive, acetonitrile / chloroform): *m/z*: 1946.63589 (M+H$^+$), calculated for $C_{124}H_{213}N_6O_{10}^+$: 1946.63377. CHN (%): calculated for $C_{124}H_{212}N_6O_{10}$: C, 76.49; H, 10.97; N, 4.32; found: C, 76.23; H, 10.77; N, 4.09. UV/vis (CH_2Cl_2; $c = 1\cdot10^{-6}$ M): λ_{max} [nm] (ε [M^{-1}cm^{-1}]) = 664 (220 000).

3. ^{1}H NMR Spectrum of Donor Unit 3 and Squaraine 4

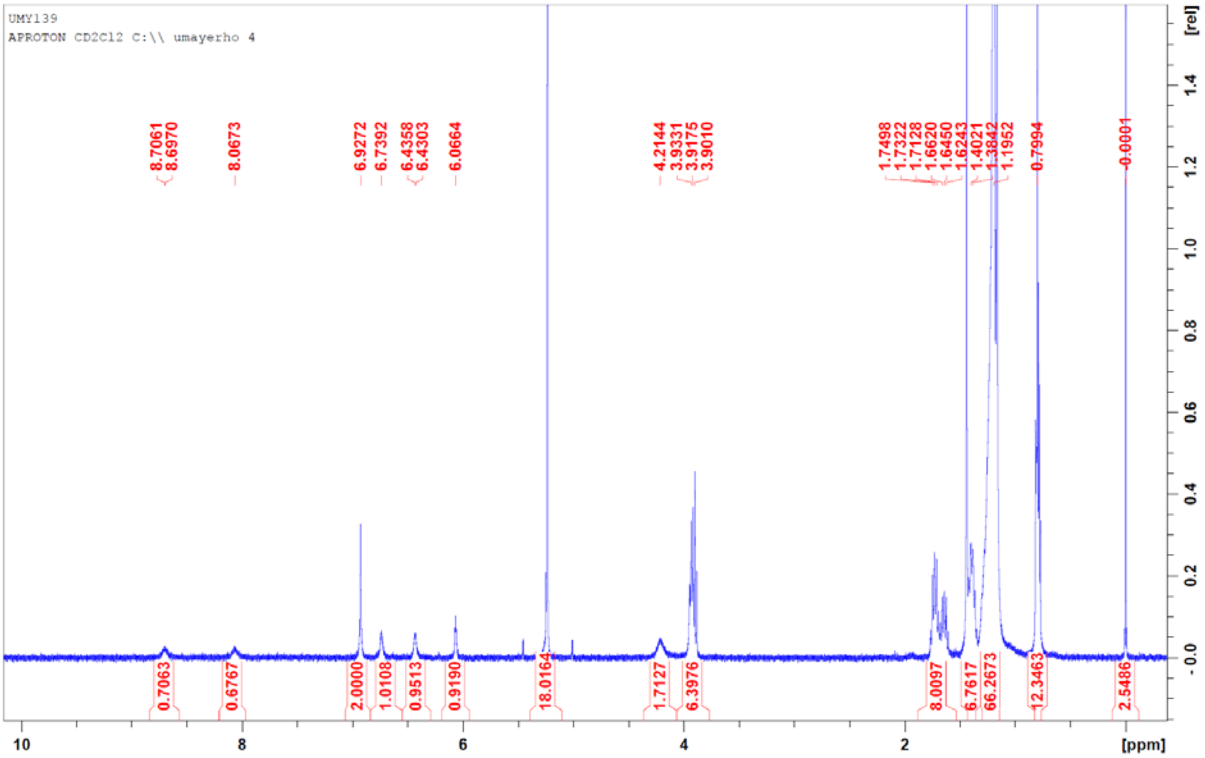


Fig. S1 ^{1}H NMR spectrum of **3** in CD_2Cl_2 (400 MHz, TMS).

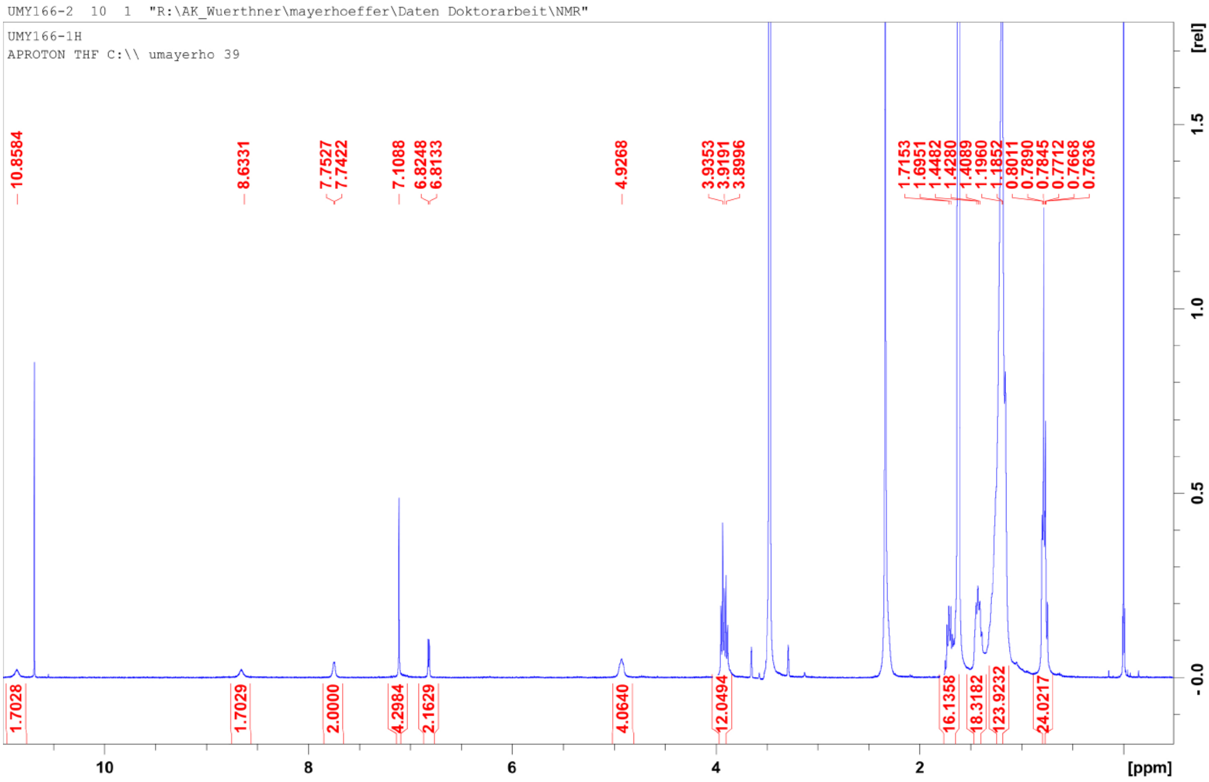


Fig. S2 ^{1}H NMR spectrum of squaraine **4** in d^8-THF (400 MHz, TMS).

4. ^{13}C and DEPT 135 NMR Spectra of Squaraine 4

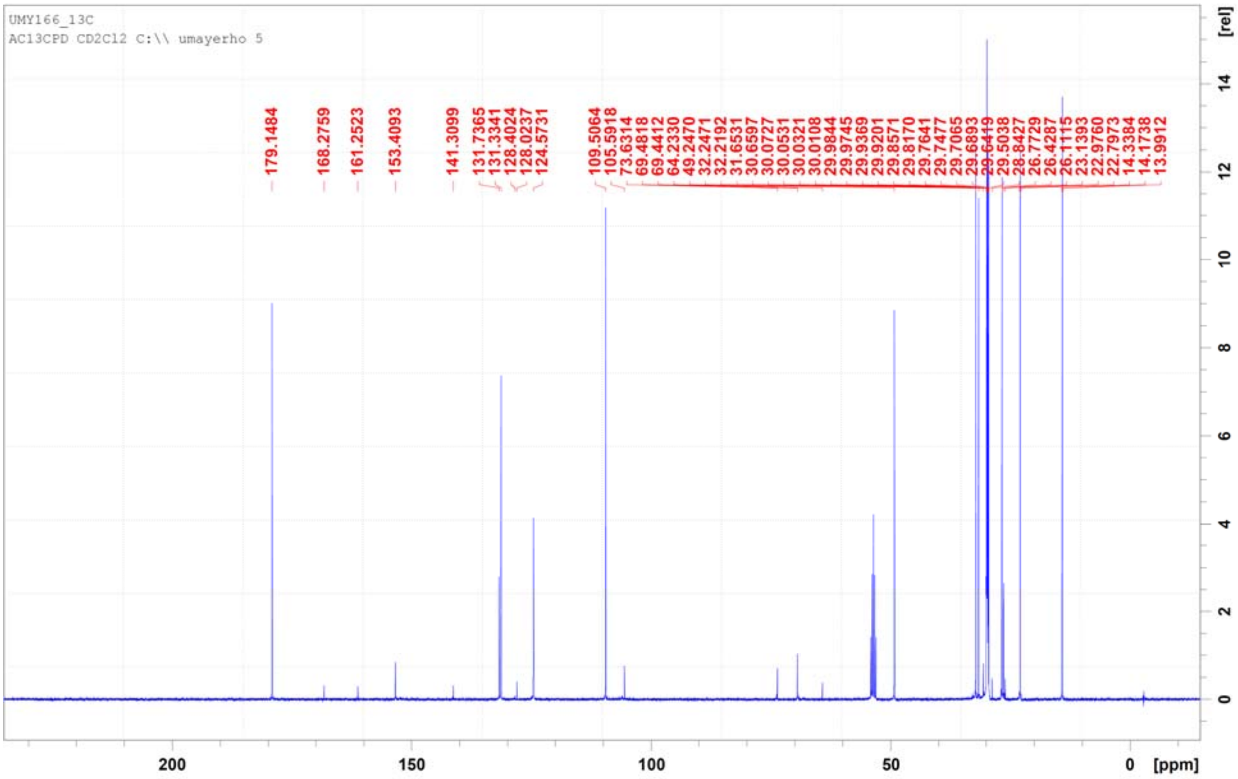


Fig. S3 ^{13}C NMR spectrum of squaraine **4** in CD_2Cl_2 (100 MHz).

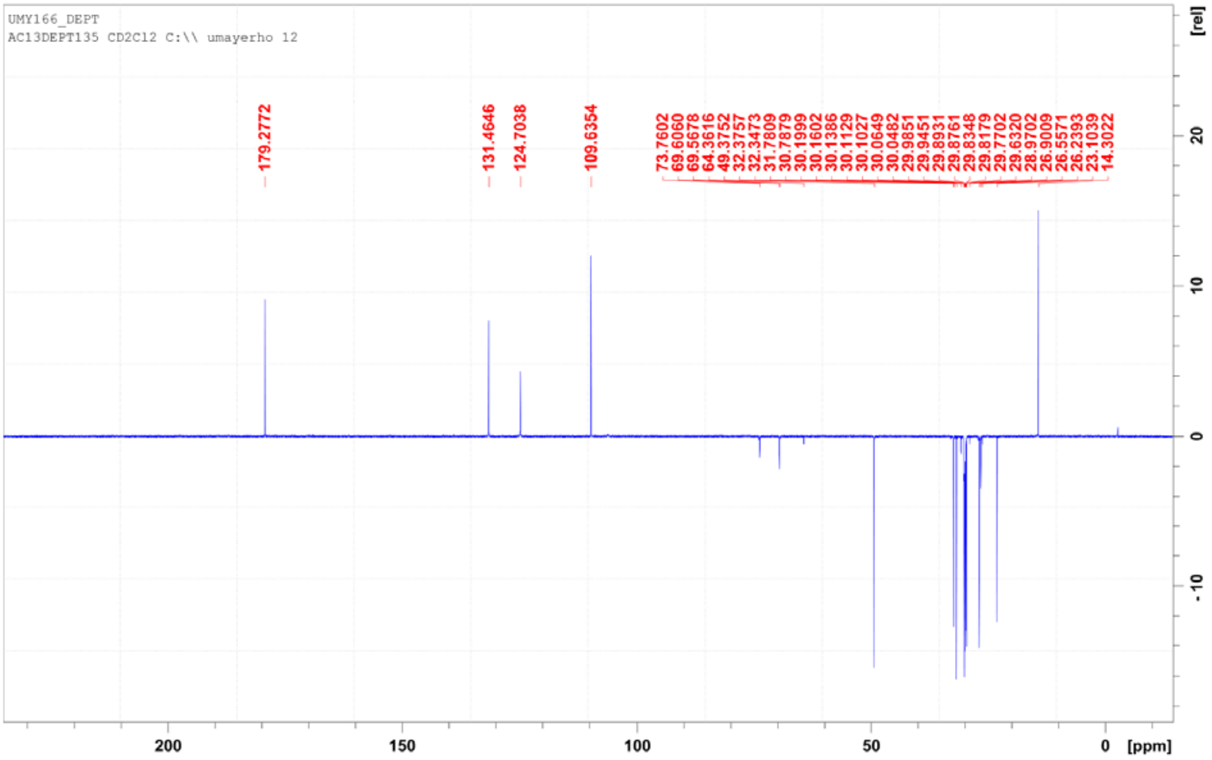


Fig. S4 DEPT 135 NMR spectrum of squaraine **4** in CD_2Cl_2 (100 MHz).

5. HRMS-ESI Mass Spectrum of Squaraine 4

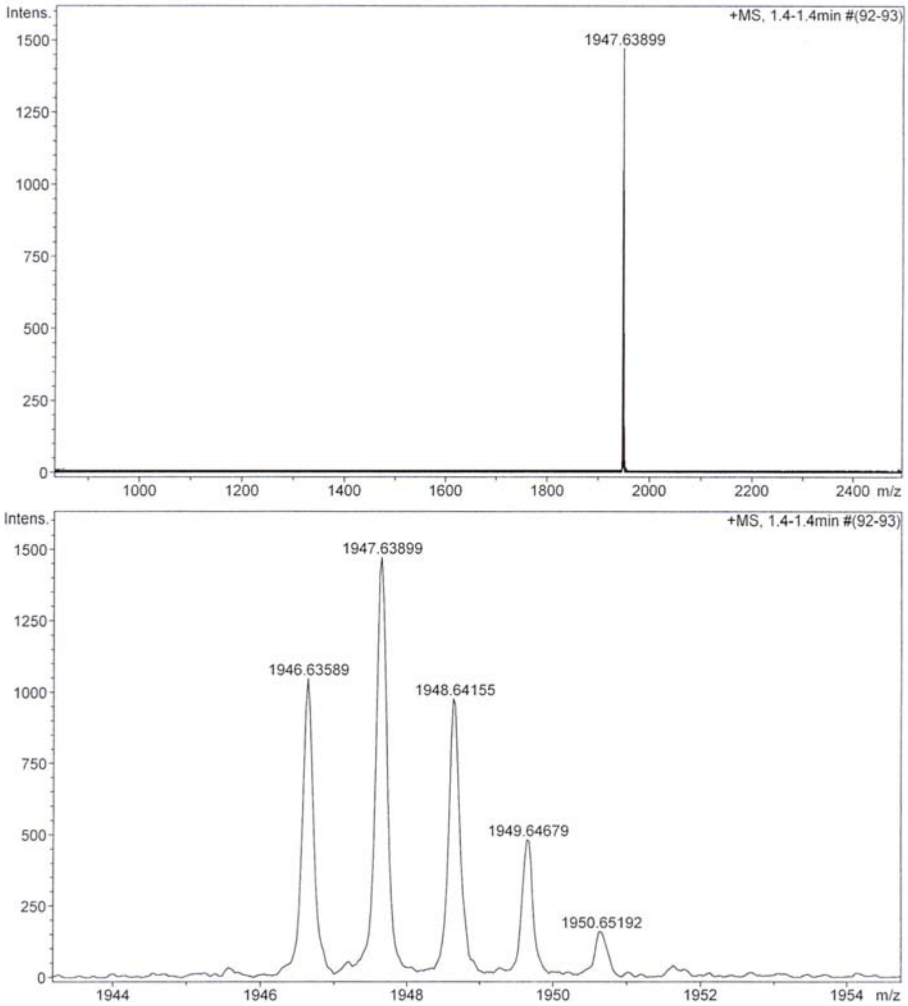


Fig. S5 ESI HRMS of squaraine **4** (positive mode, acetonitrile/chloroform).

6. Fluorescence Spectra

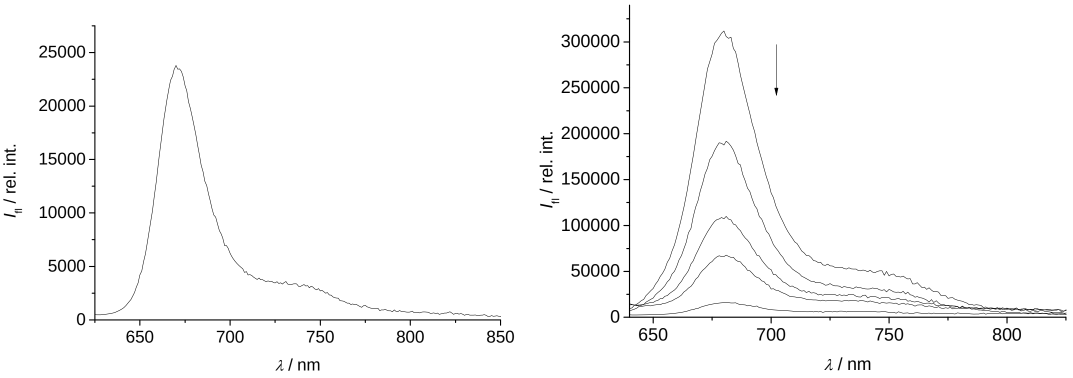


Fig. S6 Fluorescence spectra of squaraine **4** in CH_2Cl_2 (left) and in toluene (arrow indicates relative fluorescence decrease with increasing concentration from $c = 1 \times 10^{-7}$ M to $c = 1 \times 10^{-3}$ M). Excitation wavelength 590 nm.

7. Solid State UV/vis spectra

Fig. S7 shows the UV/vis absorption spectra of spin-cast films of squaraine **4** aggregates from MCH and toluene solutions in comparison with the respective absorption spectra of their aggregate solutions in the given solvents. As can be seen, these spectra are indeed very similar. In particular, the UV/vis spectra for both aggregate solutions and thin films in these two solvents exhibit almost the same band shape and absorption maxima, indicating the same excitonic interactions, and thus the same supramolecular arrangement in both solvents. In contrast, films deposited from monomeric solution in CH_2Cl_2 show different absorption spectra pointing at a different presumably less defined arrangement suggesting the presence of an amorphous solid state. However, the absorption spectra of the film cast from CH_2Cl_2 change with the time, indicating a rearrangement of the dyes in the solid state that seems to lead to the same aggregate type as observed upon casting of aggregate solutions from toluene and MCH.

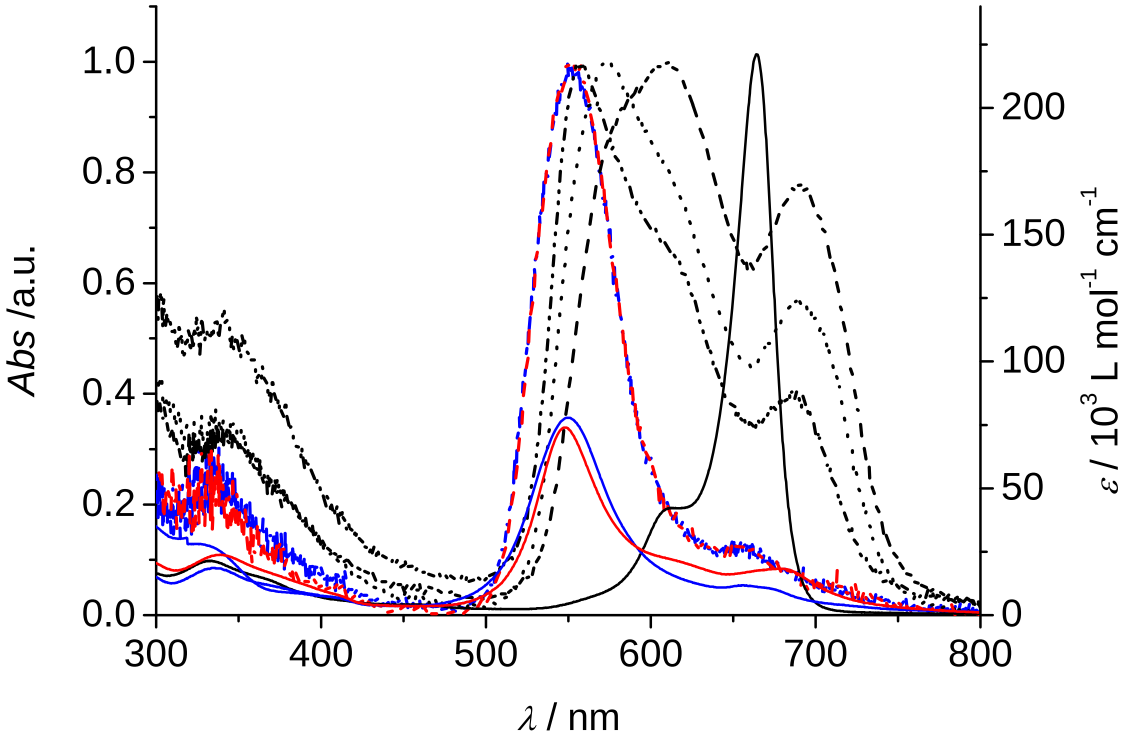


Fig. S7. Solvent-dependent UV/vis absorption spectra (solid lines) of squaraine **4** in CH_2Cl_2 (black; $c = 1 \times 10^{-3}$ M, 25 °C), toluene (blue; $c = 1 \times 10^{-3}$ M, 25 °C), and MCH (red; $c = 1 \times 10^{-5}$ M, 25 °C) and their corresponding UV/vis absorption spectra in thin films spin-casted from the above solutions: CH_2Cl_2: as-cast (black dashed line), after 48 h (black pointed line), and after 14 d (black dashed-pointed line); toluene (blue dashed line); MCH (red dashed line).

8. Self-assembly Studies

8.1 Derivation of the equations

Determination of the degree of aggregation from UV/vis/NIR data:

From the concentration- as well as the temperature-dependent UV/vis/NIR measurements, the degree of aggregation α was calculated according to eqns (S1) and (S2), respectively.

$$\alpha(c) = \frac{\varepsilon(c) - \varepsilon_{\mathrm{M}}}{\varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{M}}} \tag{S1}$$

and

$$\alpha(T) = \frac{\varepsilon(T) - \varepsilon_{\mathrm{M}}}{\varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{M}}} \tag{S2}$$

Where $\varepsilon(c)$ is the measured apparent absorption coefficient at concentration c and $\varepsilon(T)$ is the measured apparent absorption coefficient at temperature T. ε_{M} and ε_{A} are the respective absorption coefficients of the monomer (M) and fully aggregated state (A). They could directly be determined from the spectroscopic data or by extrapolation of the measured apparent absorption coefficient to their asymptotic value at high and low concentration and temperature, respectively.

8.2 Additional UV/Vis spectroscopic data

UV/vis/NIR absorption spectra in different solvents:

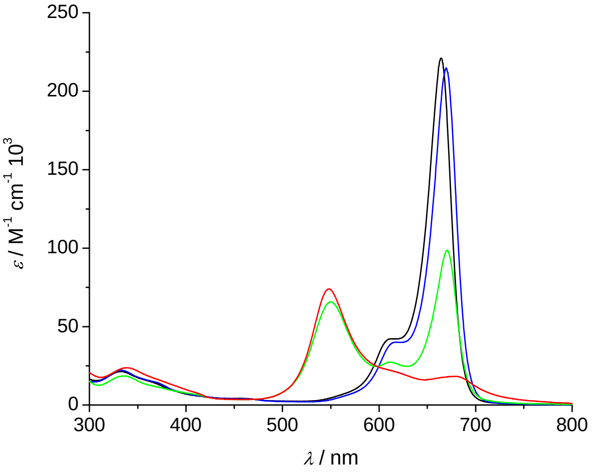


Fig. S8 Solvent-dependent UV/vis absorption spectra of squaraine **4** ($c = 1 \times 10^{-5}$ M, 25 °C) in CH_2Cl_2 (black), THF (blue), toluene (green), and MCH (red).

UV/vis/NIR aggregation studies in MCH:

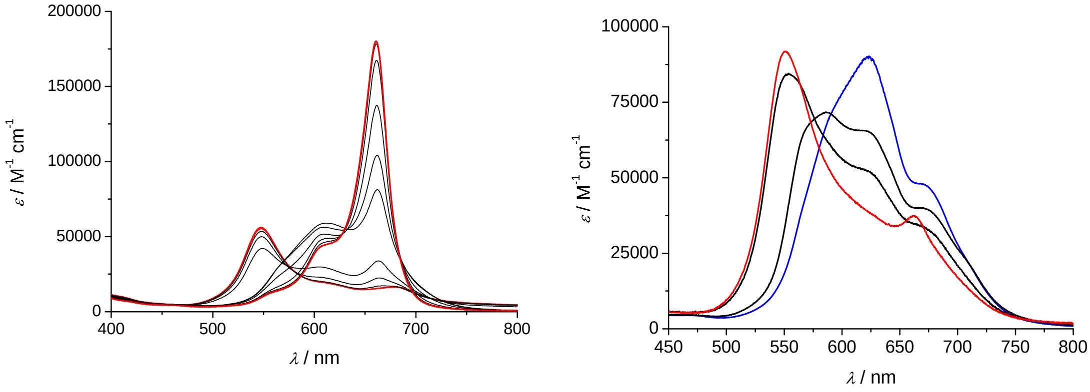


Fig. S9 Left: Temperature-dependent UV/vis/NIR absorption spectra of squaraine **4** in MCH between 0 °C and 85 °C ($c = 1\ \mathrm{x}\ 10^{-5}$ M). Right: Time-dependent UV/vis/NIR absorption spectra of squaraine **4** in MCH ($c = 1\ \mathrm{x}\ 10^{-5}$ M). The solution was first heated to 85 °C and then cooled down to room temperature, and subsequently measured in different time intervals over 48 h (t = 0 h: blue line; t = 48 h: red line).

In MCH the aggregation strength is increased, leading to the formation of kinetically trapped aggregate species. As shown in Fig. S5 (right), the transformation into the thermodynamic aggregate species is rather slow and proceeds over a period of several days.

Additional UV/vis/NIR concentration-dependent aggregation studies in toluene:

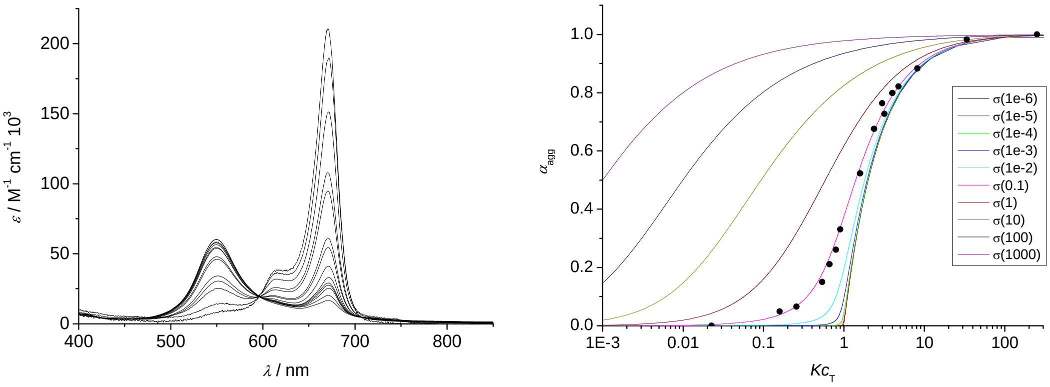


Fig. S10 Left: Second set of concentration-dependent UV/vis/NIR absorption measurements of squaraine **4** in toluene. Right: Fraction of aggregated species α_{agg} plotted as function of Kc_{T} with different σ values according to the cooperative growth model for the UV/vis concentration study (Fig. S6) at 670 nm (black points) for **4** in toluene at 20 °C.

9. FTIR Spectra

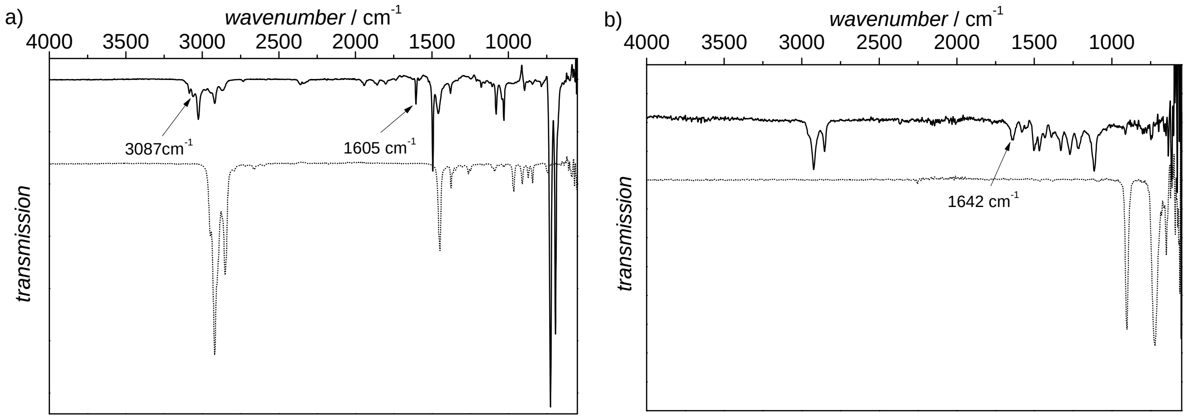


Fig. S11 a) FTIR spectrum of MCH (dotted line) and a solution of squaraine **4** (10^{-3} M) in MCH (solid line) at 25 °C; b) FTIR spectrum of $CDCl_3$ (dotted line) and a solution of squaraine **4** (10^{-3} M) in $CDCl_3$ (solid line) at 25 °C.

10. Dynamic Light Scattering

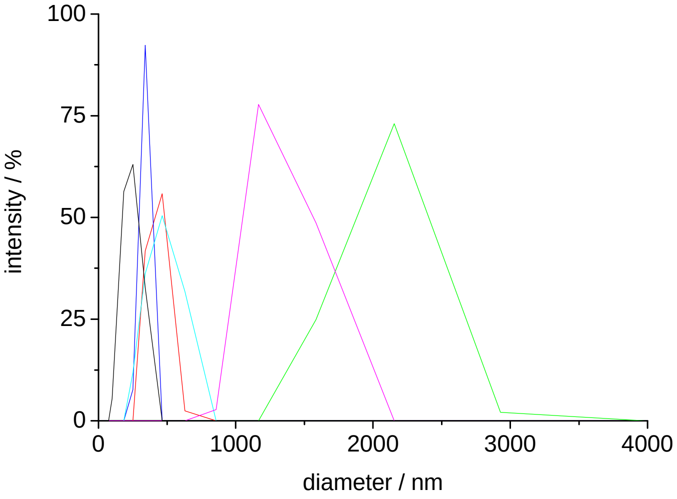


Fig. S12 Angle-dependent intensity distribution obtained by dynamic light scattering experiments of **4** in toluene (black: 90°; blue: 14°; red: 10°; cyan: 26°; magenta: 66°; green: 20°) at 20 °C.

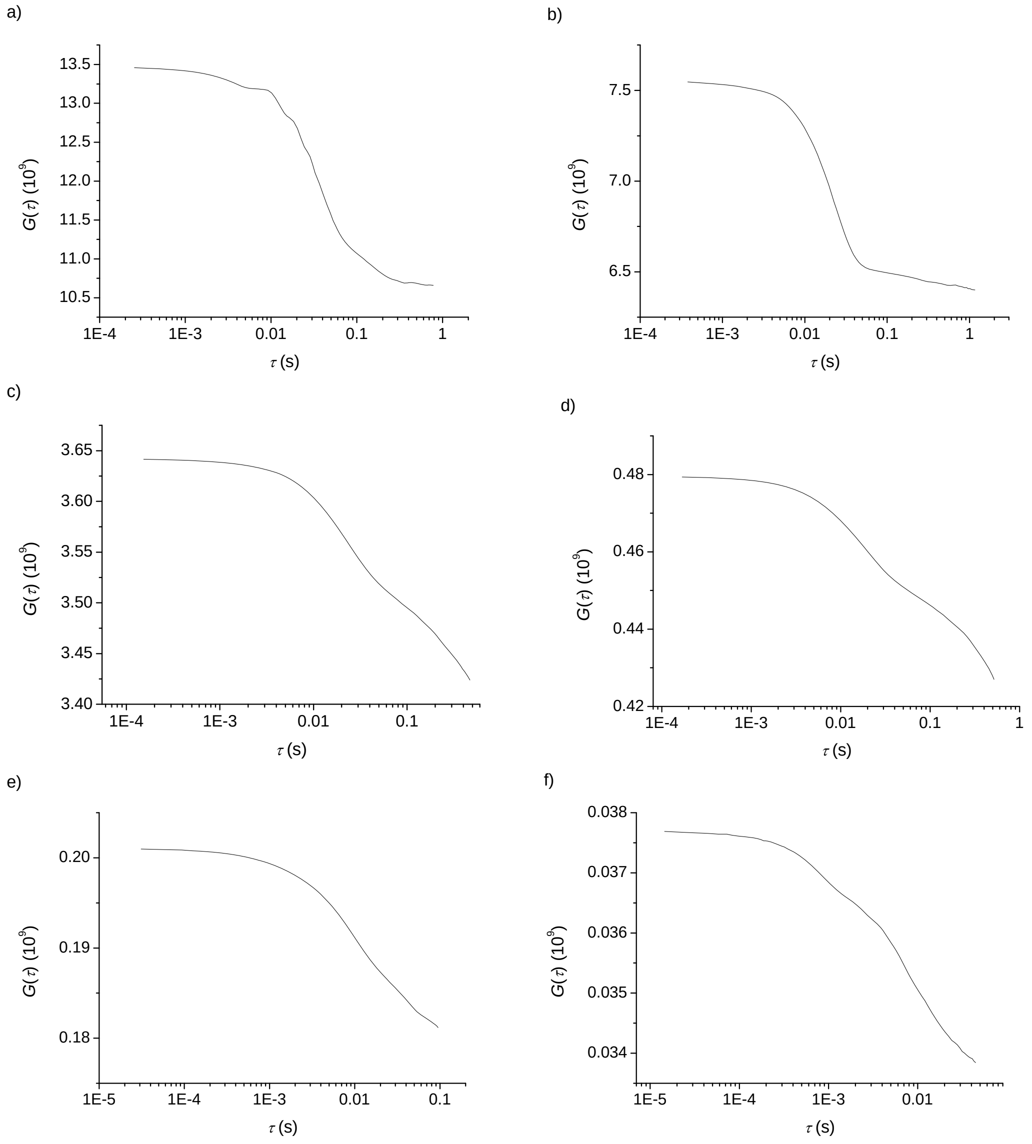


Fig. S13 Autocorrelation functions $G(\tau)$ of **4** in toluene solution (293 K) plotted against the delay time τ for scattering angles a) 10°, b) 14°, c) 20°, d) 26°, e) 66°, and f) 90°.

11. AFM Image of Squaraine 4

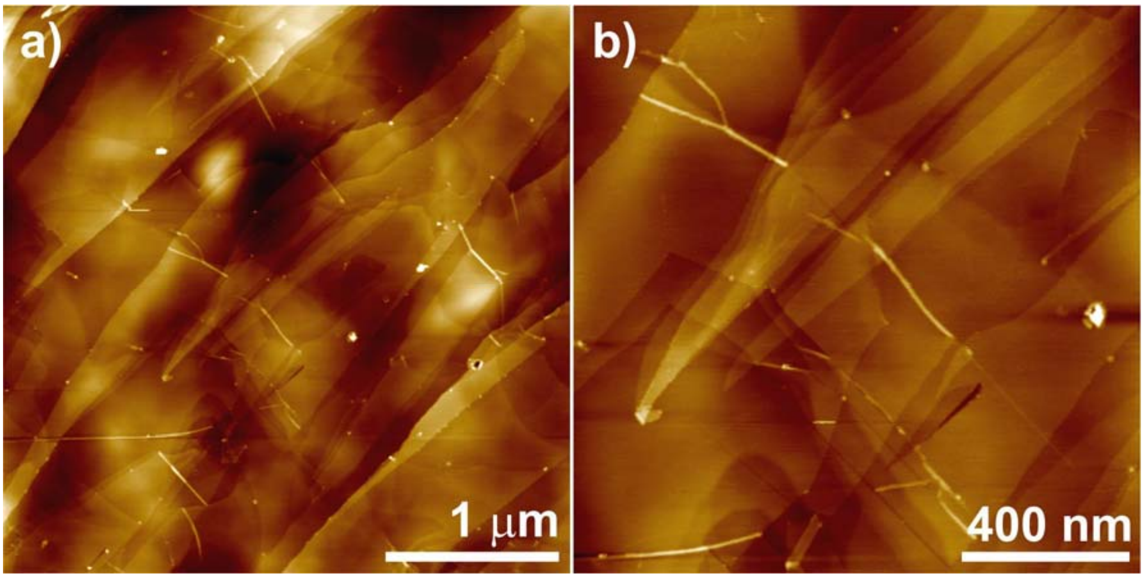


Fig. S14 a), b) AFM images of samples spin-coated from a MCH solution of **4** ($c = 5 \times 10^{-4}$ M, 5000 rpm) on HOPG.

12. SEM Image of Squaraine 4

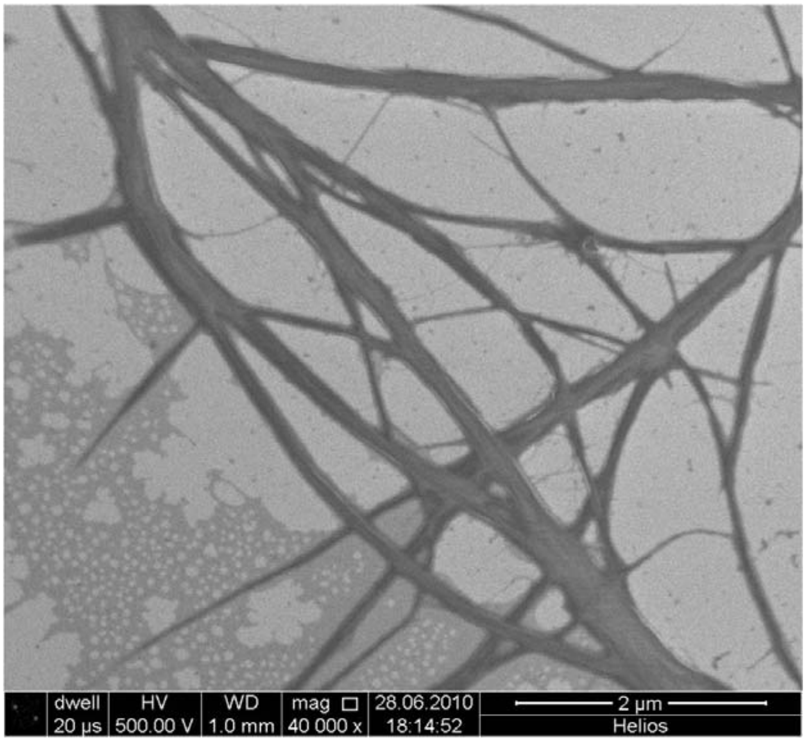


Fig. S15 SEM image of a toluene solution of squaraine **4** ($c = 1 \times 10^{-3}$ M).

13. Additional References

S1 (a) M. H. Klingele and S. Brooker, *Eur. J. Org. Chem.*, 2004, 3422; (b) F. Silvestri, M. D. Irwin, L. Beverina, A. Facchetti, G. A. Pagani and T. J. Marks, *J. Am. Chem. Soc.*, 2008, **130**, 17640.