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NIR-emitting squaraine J-aggregate nanosheets

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Click chemistry and Yamamoto coupling afforded a S-shaped π scaffold composed of two directly connected dicyanomethylenesubstituted squaraine dyes. This bis(squaraine) self-assembles into nanosheets in a cooperative self-assembly process, affording an absorption maximum at 886 nm and a fluorescence at 904 nm due to strong J-type exciton coupling.

More than 80 years after their discovery,^{1,2} J-aggregates enjoy an ever-increasing popularity. The reason might be that Jaggregates provide the most obvious example for an emergent functionality upon molecular assembly.^{3,4} Thus, depending on the respective dyes, e.g. cyanines,⁵ chlorins,⁶ bodipys,⁷ rylene bisimides, $^{\rm 8,9}$ squaraines, $^{\rm 10}$ bathochromic shifts into the NIR spectral range, fluorescence enhancement, light harvesting, and exciton migration are commonly observed and utilized for numerous fundamental studies and applications. Nevertheless, for the supramolecular chemists the required slip-stack arrangement to realize J-type exciton coupling^{11,12} imposes a challenge because most dyes prefer to stack co-facially,13 leading to H-aggregates with blue-shifted absorption bands and a guenched fluorescence.¹⁴ Indeed, supramolecular design of Jaggregates remains scarce and presumably the majority of Jaggregates were discovered by serendipity.

With regard to applications and supramolecular design, squaraine dyes^{15,16} are particularly promising and indeed for this class of dyes a significant number of functional solid state materials for electronic,¹⁷ photovoltaic^{18,19} photonic²⁰ and imaging²¹ applications take advantage of J-coupled squaraine chromophores. Here, the donor-acceptor-donor sequence implemented in the squaraine π -scaffold directs slipped-stack packing arrangements where donor and acceptor subunits of adjacent dyes are in close π - π -contact (Figure 1, right). Unfortunately, the combined structure-directing impact of



Fig. 1. Molecular structure and electrostatic potential energy surface of the squaraine scaffold utilized in this work (top) and packing arrangements (bottom) expected for squaraine dyes from the competition between dispersion (left) and electrostatic plus charge transfer (right) forces, leading to either H- (left) or J-aggregates (right).

weak compared to dispersion forces to direct the slipped-stack arrangement also for aggregates in solution, that almost exclusively show blue-shifted absorption bands due to the Htype coupling associated with co-facial stacking arrangements (Figure 1, left).^{22,23,24} This motivated us to consider more elongated molecules composed of two squaraine dyes. As we will show in the following, self-assembly of bis(squaraine) dye **BisSQ1** indeed affords the highly desired squaraine J-aggregates in solution.

The synthesis of bis(squaraine) dye **BisSQ1** is shown in Scheme 1. As a first step, semisquaraine **3** was generated via condensation reaction of 1,2-diethoxycyclobutenedione with literature known 2-methyl-3-propargylbenzothiazolium bromide.²⁵ Compound **3** was further reacted with malononitrile to incorporate the dicyanomethylene moiety, followed by condensation reaction with benzothiazolium salt **5a** to afford the unsymmetric squaraine **6a**. Subsequent copper-catalysed click reaction with azide **7** containing a hydrophilic oligoethyleneglycol (OEG) side chain provided amphiphilic squaraine **8a**. Finally, Ni-catalysed Yamamoto coupling afforded

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⁺ Electronic Supplementary Information (ESI) available: Experimental and synthetic details, UV/vis and fluorescence spectra, quantum yield correction, self-assembly studies, AFM images and proposed packing model. See DOI: 10.1039/x0xx00000x

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Scheme 1. Syntheses of squaraine SQ1 and bis(squaraine) BisSQ1. TBTA = tris(benzyltriazolylmethyl)amine; THF = tetrahydrofuran; COD =

the target bis(squaraine) **BisSQ1**. The crude product was purified by recycling gel permeation chromatography (GPC) to give pure **BisSQ1** in a yield of 42%. For details on the synthetic procedures and characterizations of all new compounds, including the monomeric reference dye **SQ1**, see the Supplementary Information.

The absorption property of **BisSQ1** was first studied under dilute condition ($c = 1 \times 10^{-5}$ M) in CHCl₃ to avoid *inter*molecular aggregation. Similar to typical squaraine dyes such as reference dye **SQ1** with C_2v symmetry,²⁶ **BisSQ1** exhibits a characteristic cyanine-like sharp and intense absorption band at long wavelengths and additional absorption bands in the UV region (300 – 450 nm) due to transitions to higher excited states (Figure 2, black line). However, in contrast to the monomeric reference dye **SQ1** with its single sharp absorption peak at λ_{max} = 703 nm (Figure 2, black dashed line), **BisSQ1** shows two peaks in the long wavelength regime, i.e. a sharp one at λ_{max} = 745 nm

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(800 cm⁻¹ red-shifted compared to **SQ1**) and a broad one at Mine 688 nm (310 cm⁻¹ blue-shifted compared to **SQ1**)^{39/D0CC03686B}

According to earlier reports for related dyes, this spectral feature arises from an equilibrium between *cisoid* folded and *transoid* S-shaped (as depicted in Scheme 1) conformations for such bis(squaraine) dyes in solution, leading to H-type (blue shift) or J-type (red shift) exciton coupling, respectively.^{27,28,29} The fluorescence spectrum of **BisSQ1** (Figure 2, red line) exhibits a small Stokes shift (180 cm⁻¹), which is common for dicyanomethylene-substituted squaraines.²⁶ However, a drastic decrease of the fluorescence quantum yield to 15% can be observed for **BisSQ1** compared to the monomeric squaraine **SQ1** (Table 1). This is in line with the low fluorescence lifetime of 1.06 ns, suggesting a more effective non-radiative decay as obvious from the calculated rate constant k_{nr} (Table 1).



Fig. 2. (a) UV/vis absorption spectra of **SQ1** (dashed black line) and **BisSQ1** (solid black line) in CHCl₃ at $c = 1 \times 10^{-5}$ M, 25 °C. The extinction coefficient c for **SQ1** was doubled for better comparison. (b) Normalized UV/vis absorption (solid black line), fluorescence (solid red line, $\lambda_{ex} = 720$ nm) and excitation (dashed blue line, $\lambda_{em} = 756$ nm) spectra of **BisSQ1** in CHCl₃ at $c = 2 \times 10^{-6}$ M, 25 °C.

In order to trigger *inter*molecular aggregation, solvents with low polarity are favoured.³⁰ Accordingly, temperaturedependent UV/vis measurement was carried out in the solvent mixture of toluene/1,1,2,2-tetrachloroethane (TCE) = 98:2 (*v*/*v*). A solution of **BisSQ1** with the concentration of 5×10^{-6} M was heated from 282 K to 358 K.[‡] At high temperature (T = 358 K), the absorption spectrum (red line in Figure 3a) exhibits an absorption maximum at 760 nm and a band shape similar to those observed in the better solubilizing solvent chloroform at room temperature (Figure 2, black line). In contrast, at low temperature (T = 282 K), a largely red-shifted band at

Table 1. Summarized optical data of SQ1 and BisSQ1 in CHCl ₃ .								
	λ _{max} (nm)	$arepsilon_{max}$ (M ⁻¹ cm ⁻¹)	λ _{em} (nm)	$\Delta^{ ilde{ u}_{Stokes}}$ (cm ⁻¹)	Ф _{FL} ^a (%)	τ _{FL} b (ns)	k _{FL} ^c (10 ⁸ s ^{−1})	k _{nr} ^c (10 ⁸ s ⁻¹)
SQ1	703	150000	724	410	79 ± 0.36 (81 ± 0.17)	4.78 ± 0.01	1.65 ± 0.01 (1.69 ± 0.01)	0.44 ± 0.02 (0.40 ± 0.01)
BisSQ1	745	255000	756	180	14 ± 0.18 (19 ± 1.5)	1.06 ± 0.01	1.32 ± 0.03 (1.79 ± 0.16)	8.11 ± 0.12 (7.64 ± 0.25)

^a Fluorescence quantum yield was determined by a calibrated integrating sphere system. The value corrected from re-absorption are given in brackets (see ESI).

^b τ_{FL} was determined by tail fit analysis of the data obtained from time-correlated single photon counting measurements with ps laser diode at 670 nm using a magic angle setup.

^c Determined according to $k_{FL} = \Phi_{FL}/\tau_{FL}$ and $k_{nr} = 1/\tau_{FL} - k_{FL}$. The value calculated from corrected QY is given in brackets.

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 λ_{max} = 886 nm is observed (blue line in Figure 3a), indicating a pronounced J-type exciton coupling due to *inter*molecular aggregation. This red-shift of 1870 cm⁻¹ compared to the dissociated state for **BisSQ1** in the same solvent at 358 K is indeed among the largest shifts observed for J-aggregates. Compared to the monomeric reference dye **SQ1** the shift is even larger (2680 cm⁻¹). Notably, a defined isosbestic point is present at 788 nm, revealing an equilibrium between only two species.



Fig. 3. (a) Temperature-dependent UV/vis spectra of **BisSQ1** in toluene/TCE 98:2 (ν/ν) at $c = 5.0 \times 10^{-6}$ M, 282 – 358 K. The arrows indicate the spectral changes with increasing temperature. (b) Plot of fractions of aggregate at 886 nm against temperature and fitting with the nucleation-elongation model.³¹

The degree of aggregation was calculated from the experimental data at 886 nm and plotted against the temperature (for details, see Supplementary Information). To analyse the self-assembly process, we have made use of the nucleation-elongation model of Meijer, Schenning and Van der Schoot.³¹ For temperatures below the elongation temperature, we could accurately fit the experimental data to the elongation regime (Figure 3b) with $R^2 = 0.9998$. At the given concentration of 5×10^{-6} M, the enthalpy release during the elongation process ($\Delta H_{\rm e}$) and the elongation temperature ($T_{\rm e}$) were calculated to be -46 KJ/mol and 342 K, respectively. For temperatures above the elongation temperature, the dimensionless equilibrium constant K_a of the activation step at the elongation temperature was estimated to be 0.087. The low value of this constant is suggestive of a high degree of cooperativity for this self-assembly process.³²

The same spectral changes could also be observed in concentration-dependent experiments, where dilution from $c = 1 \times 10^{-4}$ to 2×10^{-7} M at 298 K led to a transition from aggregated to monomeric species (Figure S6). The experimental data could be properly fitted with the cooperative K_2/K model,³³ where the results are in good agreement with the temperature-dependent measurements (for detailed analysis, see Supplementary Information).

Since the UV/vis measurements imply the formation of aggregates with strong J-type coupling which are expected to exhibit a non-forbidden, i.e. fluorescent, lowest excited state, we investigated the emission properties of the **BisSQ1** aggregate. As shown in Figure S8, indeed a weak emission was detected at 904 nm ($\lambda_{ex} = 820 \text{ nm}$, $\Delta \tilde{v}_{stokes} = 225 \text{ cm}^{-1}$). It is important to point out that the monomeric state does not absorb at 820 nm; therefore, only the aggregated state was

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excited. To further confirm the origin of 1the 3emission 5888 excitation spectrum was recorded (Figure S8, dashed blue line, $\lambda_{FL} = 1000 \text{ nm}$) where no contribution from the monomeric state exists. Despite the distortion of the band shape due to some inevitable re-absorption in order to realize a fully aggregated state, the maximum of the excitation curve agrees well with the absorption curve. Namely, by exciting only the aggregated state, an emission takes place, confirming the J-aggregate excitonic characteristic.³⁴

To gain further insight into the aggregate structure, we performed diffusion ordered spectroscopy (DOSY) NMR measurements in solution. However, a clear interpretation of the data was not possible due to an aggregate size distribution (for details, see Supplementary Information). Therefore, atomic force microscopy (AFM) measurements were carried out. Toward this goal, a solution of **BisSQ1** in toluene/TCE (98:2, *v/v*) with a concentration of 2×10^{-5} M was spin-coated onto highly ordered pyrolytic graphite (HOPG) substrate, leading to sheet-like aggregates (Figure 4a, b) with a height of 2.2 ± 0.1 nm (Figure 4c). This is in good agreement with the dimension of the molecules considering the flexibility of the side-chains (Figure S13).



Fig. 4. Height (a,b) AFM images of sample **BisSQ1** prepared by spincoating of toluene/TCE 98:2 (v/v) solution on HOPG. *Z* scale is 8 nm. Image (c) shows the cross-section analysis from yellow dashed line in image (a) and (d) a tentative packing model with hydrophobic squaraines in violet and hydrophilic oligoethyleneglycol chains in cyan.

The width of the thin sheets varies between 10-40 nm, while the length reaches up to 200 nm. Notably, similar morphology could be observed on silica wafer and hydrophilic mica surfaces (Figure S11), indicating that the structure is not influenced by the substrates. Based on the experimental data obtained from UV/vis and AFM measurements, we propose the packing model for the **BisSQ1** nanosheets shown in Figure 4d.

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Although our packing model is only tentative, it fairly well explains the strong red-shift of the absorption band due to the slipped-stack packing arrangement of **BisSQ1** molecules (Figure 4d) and the formation of lamellar sheets consisting of the hydrophobic S-shaped **BisSQ1** molecules and hydrophobic alkyl chains and the stabilization of this nanosheet against precipitation in the given solvent by solubilizing oligoethyleneglycol chains protruding above and below the sheet into the solvent phase.

Indeed, this two-dimensional sheet structure formation may be considered as a major outcome of our study. Thus, whilst onedimensional aggregation of squaraines is typically governed by dispersion forces, thereby affording co-facially stacked dyes with Htype coupling, two-dimensional aggregation as directed with our concept of extended bischromophores provides J-aggregates. This is most likely induced by the structural distortion between the chromophores with a similar brickwork type organization as observed in many thin film squaraine aggregates.¹⁷⁻²⁰ We also like to emphasize that the aggregation process in our study was accomplished in an organic solvent and not in water, where hydrophobic effects play an important role and for which indeed some larger colloidal squaraine aggregates showed J-type features.^{10,35,36, 37}

In a particular nice but rather special case Belfield and coworkers could direct such J-aggregation by the interaction of appended cationic pyridinium units by templating with polyanionic poly(acryclic acid).²¹

In conclusion, we have introduced a very simple but efficient approach to direct squaraine dye aggregation in solution from the very common cofacial stacking leading to H-type exciton coupling to the more desired slipped-stack packing leading to Jtype exciton coupling by simply connecting two dyes in a headto-tail bischromophore structure. It will be interesting to see if this simple concept can be applied also to other squaraines or even to entirely different chromophores.

Conflicts of interest

There are no conflicts to declare.

Notes and references

[‡] Aggregation of reference dye **SQ1** is too weak to be observed in our comparative concentration-dependent experiments (see Figure S4 in the Supplementary Information).

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The self-assembly of a newly synthesized bis(squaraine) dye was investigated revealing the formation of J-type aggregates with absorption maxima at 886 nm.