GDCh

Self-Assembly

 How to cite:
 Angew. Chem. Int. Ed. 2021, 60, 7851-7859

 International Edition:
 doi.org/10.1002/anie.202015390

 German Edition:
 doi.org/10.1002/ange.202015390

Tweaking a BODIPY Spherical Self-Assembly to 2D Supramolecular Polymers Facilitates Excited-State Cascade Energy Transfer

Gourab Das, Sandeep Cherumukkil, Akhil Padmakumar, Vijay B. Banakar, Vakayil K. Praveen,* and Ayyappanpillai Ajayaghosh*

In memory of Professor M. V. George

Abstract: Excited state properties such as emission, exciton transport, electron transfer, etc., are strongly dependent on the shape, size and molecular arrangement of chromophore based supramolecular architectures. Herein, we demonstrate creation and control of distinct supramolecular energy landscapes for the reversible control of the excited-state emission processes through cascade energy transfer in chromophore assemblies, facilitated by an unprecedented solvent effect. In methylcyclohexane, a tailor-made Y-shaped BODIPY derivative selfassembles to form an unusual spherical architecture of 400-1200 nm size, which exhibits a single emission at 540 nm upon 475 nm excitation through a normal excitation deactivation process. However, in n-decane, the same BODIPY derivative forms two-dimensional supramolecular sheets, exhibiting multiple emission peaks at 540, 610, 650, 725 and 790 nm with 475 nm excitation due to cascade energy transfer. Further control on the morphology and excitation energy transfer is possible with variable solvent composition and ultrasound stimulation, resulting in enhanced near-infrared emission with an overall pseudo Stokes shift of 7105 cm^{-1} .

Introduction

Creation of supramolecular architectures of different shapes, sizes and properties is the fundamental step to realize next generation complex multi-component systems with specific functions and applications.^[1] In this context, chromophore based supramolecular systems have been at the center stage due to their reversible optoelectronic properties that can be modulated through the molecular assembly.^[2] In recent times, several approaches have been introduced for the controlled assembly of π -conjugated molecules.^[3-5] Living supramolecular polymerization,^[3,5a] crystallization-driven

```
[*] G. Das, Dr. S. Cherumukkil, A. Padmakumar, V. B. Banakar,
Dr. V. K. Praveen, Prof. Dr. A. Ajayaghosh
Photosciences and Photonics Section, Chemical Sciences and
Technology Division, CSIR-National Institute for Interdisciplinary
Science and Technology (CSIR-NIIST)
Thiruvananthapuram, Kerala 695019 (India)
E-mail: vkpraveen@niist.res.in
ajayaghosh@niist.res.in
G. Das, A. Padmakumar, Dr. V. K. Praveen, Prof. Dr. A. Ajayaghosh
```

Academy of Scientific and Innovative Research (AcSIR) Ghaziabad, Uttar Pradesh 201002 (India) self-assembly^[6] and seeded supramolecular polymerization^[7] are examples that control the length and dimension of supramolecular structures through kinetic and thermodynamic control of self-assembly. While living supramolecular polymerization is undoubtedly a powerful tool for the precise control of molecular self-assembly, it cannot be applied as a general strategy. Therefore, different kinds of external stimuli such as light,^[8] pH,^[9] redox,^[10] enzyme,^[11] ultrasound,^[12] and solvents,^[13] have been exploited for controlled supramolecular polymerization of functional π -systems.^[14]

Cascade energy transfer in supramolecular architectures is a fundamentally important process applicable to the biological and materials world.^[15] For example, the phycobilisomes, which is the major light-harvesting complex in cyanobacteria and red algae, is considered one of the most efficient light-harvesting systems with more than 95% efficiency due to the cascade energy transfer.^[15a,e] Though inferior to natural light-harvesting systems, the artificial supramolecular systems, due to the presence of aggregates of varying energy levels with large anisotropy, provides ample opportunities to simulate the natural light-harvesting processes. In this context, molecular assemblies of certain chromophores having the mixture of aggregates with different levels of electronic coupling have been shown to facilitate cascade energy transfer leading to red-shifted emission.^[16] This red-shift can lead either to a broad emission, if aggregates of closely matching energy levels are involved or to multiple emission if aggregates of discrete energy levels are present in the hierarchical self-assembly. However, the latter type of molecular assembly resulting in multiple emission covering the entire visible-NIR region upon a single excitation remains a challenge.

Among different chromophores, 4,4-difluoro-4-bora-3a-4a-diaza-s-indacene (BODIPY) is an excellent choice for creating supramolecular optoelectronic materials due to their photostability, high molar absorptivity and sensitive fluorescence features.^[17-20] Here, we demonstrate how distinct energy landscapes can be obtained by creating different morphological features that facilitate reversible modulation of emission behavior. This is possible by tweaking the selfassembly of *meso* π -extended BODIPY dyes **1–3** (Figure 1 a) with solvents as established in this work. The high ground state dipole moment ($\mu_g = 7.53$ D) of Y-shaped **1** and **2** drives the self-assembly in cyclic nonpolar solvents such as methylcyclohexane (MCH) or *trans*-decalin, initially resulting in 10– 20 nm spheres, which transform into large spheres of 600– 800 nm with time as confirmed by dynamic light scattering

Supporting information and the ORCID identification number(s) for
 the author(s) of this article can be found under https://doi.org/10.
 1002/anie.202015390.



Figure 1. a) Molecular structures of the Y-shaped BODIPY derivatives 1–3. b) Absorption (between 420–580 nm corresponding to the BODIPY chromophore) and c) normalized emission spectra (λ_{ex} =475 nm) of 1 in chloroform (1×10⁻⁴ M), MCH, *trans*-decalin (3×10⁻⁴ M) and *n*-decane, *n*-heptane (3×10⁻⁴ M). Deconvoluted d) absorption and e) emission spectra of 1 in *n*-decane at 506 and 610 nm, respectively. f) The plot of α_{agg} versus temperature at different concentrations of 1 in *n*-decane; α_{agg} was calculated by monitoring the absorbance changes at 530 nm. Inset shows the van't Hoff plot obtained through the controlled cooling experiments of 1 in *n*-decane. DLS size distribution of 1 in MCH (3×10⁻⁴ M): g) immediately after fast cooling, h) after aging the sample for 24 h, and i) after cooling at a controlled rate of 1 K min⁻¹.

(DLS) experiments. Evaporation of the MCH solution of 1 or 2 on a substrate resulted in an assembly of spherical structures, wherein each large sphere is surrounded by a layer of self-assembled nanospheres, appearing like a core-shell structure with an average size of 400-1200 nm. The spherical particles exhibited a normal emission spectrum with a single maximum at 540 nm. On the other hand, in linear nonpolar solvents such as *n*-heptane or *n*-decane, two-dimensional (2D) supramolecular sheets having broad emission comprising of 540, 610, 650, 725 and 790 nm bands are formed. Interestingly, the single and multiple emission could be reversibly controlled by tweaking the morphology between the spherical and 2D assemblies by changing the solvent composition. Molecule 3 having short alkyl chains failed to form either the spherical morphology or 2D sheets, revealing the importance of the alkyl chains in the self-assembly process. Ultrasound stimulation of the 2D sheets exhibited better efficiency for the successive energy transfer as evident by a 2.2-fold increase in the intensity of the near infrared (NIR) bands at 725 and 790 nm. The morphological features and the associated emission behavior described here are unprecedented and the origin of multiple emission ascribed is the manifestation of a cascade effect of the excitation energy as established by time-resolved emission and anisotropy studies.

Results and Discussion

After synthesizing 1-3 (Scheme S1-S3), we have studied their optical behavior and self-assembly processes (Figure 1 b,c and Figure S1). In CHCl₃ $(1 \times 10^{-4} \text{ M})$ at 295 K, the UV-vis absorption spectrum exhibited two maxima at 290 and 504 nm with a shoulder band around 475 nm. The broad absorption observed at 290 nm ($\varepsilon = 5.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) corresponds to the phenyleneethynylene moiety, whereas the narrow absorption feature at 504 nm ($\varepsilon = 1.3 \times 10^5 \,\mathrm{M^{-1} \, cm^{-1}}$) implies the strong $S_0 \rightarrow S_1$ electronic transition involving $(0 \rightarrow$ 0) vibrational states of the BODIPY chromophore. The band at 475 nm can be considered as the vibronic shoulder of S_0 - S_1 transition.^[20] On the other hand, the absorption spectrum of $1 (3 \times 10^{-4} \text{ M})$ in MCH or *trans*-decalin, when heated to 363 K followed by cooling to 283 K at a rate of 1 K min⁻¹, exhibited an absorption maximum at 288 nm ($\varepsilon = 6.75 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), with a broad band ($\lambda_{max} = 504 \text{ nm}, \epsilon = 1.04 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) between 420–550 nm. Furthermore, 1 exhibits an emission maximum at 520 nm ($\Phi_{\rm F} = 0.39$) in CHCl₃, whereas in MCH a red-shifted maximum at 540 nm ($\Phi_{\rm F} = 0.20$). These observations indicate aggregation of 1 in MCH as further confirmed by temperature-dependent ¹H NMR, absorption and emission studies (Figures S2 and S3). Upon gradual reduction in temperature from 363 to 283 K, the intensity of the absorption maximum was reduced and the absorption spectrum corresponding to both BODIPY and phenyleneethynylene part became broad (Figure S3a). In contrast, the temperature-dependent emission studies showed a gradual increase in the intensity when 1 in MCH was cooled from 363 to 283 K, indicating aggregation-induced enhanced emission behavior (Figure S3b).^[2a,21a] Since the phenyl ring attached at the *meso* position of BODIPY chromophore 1 is unsubstituted, rotational and vibrational motions are facilitated at higher temperature, leading to non-radiative deactivation of the excited state and less emission.^[20a] However, upon gradual reduction in temperature, aggregation of 1 restricts the rotation and vibrational motion and activates radiative excited state decay to display enhanced emission. Aggregation of **1** in MCH at a concentration of 3×10^{-4} M was further confirmed from the plot of the fraction of aggregates (a_{agg}) of 1 with respect to temperature, revealing a non-sigmoidal cooling curve, which is characteristic of a co-operative selfassembly process (Figure S3c and Table S1).^[21]

In *n*-decane or *n*-heptane $(3 \times 10^{-4} \text{ M})$, the absorption spectra of 1 within 230-420 nm was almost similar to those in CHCl₃ and MCH (Figure S1), however, the absorption corresponding to the BODIPY chromophore appeared much broader ($\lambda_{\text{max}} = 506 \text{ nm}, \varepsilon = 7.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), with predominant shoulder bands in the lower and higher wavelength region (470 and 570 nm), indicating the formation of multiple aggregates (Figures 1b and S4). Surprisingly, the emission spectrum of $1 (3 \times 10^{-4} \text{ M})$ in *n*-decane or *n*-heptane exhibited an unusually broad band with multiple maxima at 540, 610, 650, 725 and 790 nm ($\Phi_{\rm F} = 0.14$). The peak at 650 nm is more resolved in *n*-heptane (Figure 1c). Deconvolution of the broad absorption peak (506 nm) obtained in n-decane shows two peaks at 473 and 509 nm, confirming the formation of aggregates (possibly mixture of both H- and J-type aggregates) (Figure 1 d).^[22] Deconvolution of the broad emission band at 610 nm in n-decane revealed two peaks at 612 and 686 nm (Figure 1e).

These observations were further confirmed from the temperature-dependent absorption and emission studies of 1 in *n*-decane (Figure S4, S5). At 363 K, 1 in *n*-decane displayed a sharp absorption band at 504 nm, which gradually reduced its intensity and became broad at 283 K (Figure S4a). The intensity of the emission spectrum of **1** in *n*-decane was initially found to increase with an appearance of a new peak at 725 nm upon reducing the temperature 363 to 348 K (Figure S5b, upper panel). Between 343 to 313 K, the emission intensity of the peak at 552 nm was found to gradually decrease with the appearance of a new peak at 600 nm (Figure S5b, middle panel). Further reduction in temperature to 283 K resulted in an overall enhancement in the intensity of emission profile with three distinct maxima at 552, 600 and 725 nm (Figure S5b, lower panel). A similar absorption and emission changes were also noticed at various other concentrations of **1** in *n*-decane (Figure S4b–d, S5a). BODIPY derivatives are known to exhibit broad multiple emission in solid/semicrystalline powder form, however, not in any solvents.^[19f,20d,e] While MCH and *n*-decane have more or less identical polarity, except for their difference in structure and shape (cyclic and linear), the observed difference in the emission behavior in these solvents could be associated with the hierarchical assembly of the BODIPYs.

Plots of a_{agg} of **1** with respect to temperature revealed non-sigmoidal cooling curves for a wide range of concentrations $(1 \times 10^{-4} \text{ to } 3 \times 10^{-4} \text{ M})$ in *n*-decane (Figure 1 f and S4). The cooling curves thus obtained were fitted to an equilibrium model, characteristics of a co-operative selfassembly process.^[21] Details of the thermodynamic parameters related to the fitting are summarized in Table S2. The plot of the natural logarithm of the reciprocal concentration of 1 against reciprocal of $T_{\rm e}$ exhibited a linear relationship (van't Hoff plot, Figure 1 f inset). The thermodynamic parameters of **1** in *n*-decane were $\Delta H^{\circ} = -84.26 \text{ kJ mol}^{-1}$, $\Delta S^{\circ} =$ $-168.43 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$ and $\Delta G^{\circ} = -34.07 \text{ kJ} \text{ mol}^{-1}$, indicating that the self-assembly takes place through an enthalpically driven co-operative process. DLS experiments of 1 in MCH $(3 \times 10^{-4} \text{ M})$ under fast cooling revealed the existence of two different bands with size distributions of 10-20 nm (80-90%) and 200-300 nm (10-20%) (Figure 1g). After aging for 24 h, the size of the aggregates increased to 600-800 nm (70%)while the population of the 10-20 nm size aggregates decreased to 30%, indicating a consecutive process taking place, where the initially formed smaller spherical aggregates were directly converted to bigger size assemblies without converting into the monomers (Figure 1 h).[5b] However, a slow cooled (1 Kmin⁻¹) solution exhibited almost similar size of the assemblies as obtained by aging (Figure 1i). No time-dependent changes were noticed in the case of aggregates of 1 in *n*-decane, implying that these aggregates have reached equilibrium when cooled at a controlled rate (Figure S6).

Transmission electron microscopy (TEM) images of the self-assembly in MCH $(3 \times 10^{-4} \text{ M})$ exhibited a spherical morphology akin to a core-shell type structure^[23] having broad size distributions of 400-1200 nm. The spheres from the fast-cooled solution of 1 in MCH have diameters between 400 and 600 nm (Figure 2 a,b), which upon aging for 24 h showed a size increase of 600-1200 nm (Figure 2 c,d). However, a slowly cooled solution (1 Kmin⁻¹) resulted in spherical assemblies of 400-1000 nm (Figure S7). Magnified images of the spherical structures revealed a hyperdense core region having an average diameter of 200-900 nm (Figure 2b,d and S7b) and a less dense shell region of about 100–300 nm width. While these types of structures are common in the case of inorganic semiconductors, such structures are rare in the case of organic single molecular self-assembly. The solvent evaporation on the TEM grid may result in a thick core, around which excess nanospheres present in the mixture self-assemble to form a shell. On the other hand, from n-decane solution $(3 \times 10^{-4} \text{ M})$, 2D sheet-like structures were obtained (Figure 2e,f and Figure S8). Cross-sectional analysis indicates an average height of 1.9 ± 0.1 nm with marginal surface roughness. Upon increasing the concentration of 1 in *n*-decane ($8 \times$



Figure 2. TEM images of **1** in MCH $(3 \times 10^{-4} \text{ M})$, a) immediately after fast cooling and c) after aging the sample for 24 h. b, d) Magnified images corresponding to Figure 2a and c, respectively. e) TEM and f) AFM images of **1** in *n*-decane $(3 \times 10^{-4} \text{ M})$. The height profile along the yellow line is shown in the inset of Figure 2 f. g) SEM image of the *n*-decane gel $(8 \times 10^{-3} \text{ M})$. Inset shows the photograph of the corresponding gel under the illumination of 365 nm UV light. h) The plot of dynamic storage (G', blue) and loss modulus (G'', magenta) against shear stress (σ) for *n*-decane gel $(8 \times 10^{-3} \text{ M})$ at 298 K. Frequency (ν) was kept fixed at 1 rad s⁻¹. i) Fluorescence microscopy image of the diluted *n*-decane gel.

 10^{-3} M), the nanosheets were grown into large interconnected structures leading to an orange-red emitting gel (Figure 2g-i). However, **1** failed to form a gel in MCH (Figure S9). The viscoelastic nature of the *n*-decane gel is evident from the stress sweep experiments, which revealed the dependencies of storage modulus (*G'*) and loss modulus (*G''*) on the applied shear stress. Both the *G'* and *G''* were independent of applied stress up to 5.75 Pa, indicating the substantial elastic nature of the gel (Figure 2h).^[24] These observations underpin the ability of **1** to undergo 2D supramolecular polymerization in *n*-decane.^[4,25,26]

We hypothesized that, if the emission behavior is associated with morphological features, tweaking the spherical assembly to the 2D sheets may change the single emissive state to the multi-emissive one. Addition of different volume fractions (f = v/v) of *n*-decane to **1** in MCH (3×10^{-4} M), we found the spherical structure slowly changing to elongated sheets and then to large 2D sheets (Figure 3a-d). Upon increasing f, the intensity of the absorption of the BODIPY moiety ($\lambda_{max} = 504$ nm) gradually decreased with the appearance of a shoulder band at a higher wavelength. Interestingly, we could see multiple emission peaks at 600 and 725 nm in addition to the peak at 540 nm (Figure 3e). Similarly, upon addition of MCH to 1 in n-decane, the multiple emission changed to a single emission (Figure 3 f). The reversibility in the emission feature along with the change in morphology underpins the role of the solvent-induced self-assembly^[27] in perturbing the excited state properties.^[28] Surprisingly, the intensities of the 540 and 600 nm bands were decreased while the intensity of the NIR emission band at 725 and 790 nm exhibited a 2.2 times enhancement upon sonication^[12,24a,29] of 1 in *n*-decane (Figure 3g). Similarly, the enhancement in NIR emission was also noticed when *n*-decane aggregates of 1 were cast as a film (Figure S10a). Upon sonication, the absorption intensity was slightly reduced (Figure S10b) and the formation of multilayered 2D structures was observed by TEM analysis (Figure S10c,d). In contrast, when sonication was applied to 1 aggregates in MCH, the emission profile remained almost unaltered (Figure 3h). The results of these studies indicate that sonication and film formation favor multilayered 2D assemblies of 1, which enhance the NIR emission.

A deeper understanding of the origin of the multiemission feature was possible with time-resolved emission spectral (TRES) studies of 1 in MCH and *n*-decane $(3 \times$ 10^{-4} M) (Figure 4 a-f). The emission spectra at different time scales in MCH ($\lambda_{ex} = 375 \text{ nm}$) showed an increase in the intensity at 550 nm up to 280 ps followed by a gradual decrease in the intensity while retaining the nature of the emission profile up to 2.80 ns (Figure 4a). This observation indicates a normal excitation-deactivation process (Figure 4d). However, upon excitation in *n*-decane at 375 nm, a growth profile at 555 nm was observed within 32-210 ps (Figure 4b). With further increase in timescale up to 520 ps, the 555 nm emission intensity gradually decayed with a redshift of the emission peak to 600 nm within the time scale of 950 ps. Thereafter, the emission peak at 600 nm showed a time-dependent decay up to a timescale of 2.40 ns. The timedependent decay of the emission at a lower wavelength and the growth at the higher wavelength with dynamic red-shift of the emission are characteristic of energy migration from the excited states of lower-order aggregates (higher excited state

Research Articles



Figure 3. TEM images of aggregates of 1 upon increasing the volume fractions of *n*-decane in MCH (*f*): a) f=0.02-0.05, b) f=0.25, c) f=0.75 and d) f=0.95-0.98. Figure 3 c inset shows the zoomed image. Changes in emission ($\lambda_{ex}=475$ nm) upon varying the solvent compositions: e) addition of various fractions of *n*-decane to aggregates of 1 in MCH and f) addition of various fractions of MCH to aggregates of 1 in *n*-decane (3×10^{-4} M). Emission spectra of 1 ($\lambda_{ex}=475$ nm) in g) *n*-decane and h) MCH (3×10^{-4} M), before (blue) and after (magenta) sonication.

energy) to the higher-order aggregates (lower excited state energy) leading to the multiple emission.^[16] Figure 4e reveals that within 0.17 ns, the peak intensity at 555 nm reaches a maximum and then undergoes a rapid tri-exponential decay with time constants of 1.49 ns (44.76 %), 5.82 ns (35.63 %) and 0.25 ns (19.61 %). The emission at 600 nm reaches the maximum at 0.25 ns with a negative pre-exponential. The fitted rise time value of 0.34 ns at 600 nm correlates with the 0.25 ns decay component observed at 555 nm emission, thus validating the energy migration process. Similarly, the 650 nm emission peak also reached the maximum at 0.35 ns, followed by a successive decay.

Since the multi-emissive nature is found to be strongly influenced by ultrasound, TRES analysis of the sonicated samples in n-decane was performed (Figure 4c). The initial increase in the emission profile at 555 nm within 30-160 ps exhibited a subsequent decrease in the intensity within a time scale of 390 ps, with the formation of a new red-shifted peak at 600 nm. The peak at 600 nm exhibited an increase in the emission intensity within 260-590 ps followed by a successive time-dependent decay. Within 650 ps, another peak at 725 nm (NIR region) was formed, which reached its maximum and then gradually decayed, showing a perfect correlation between 600 and 725 nm peaks, indicating energy transfer from the 600 nm emitting species. Plots of the normalized emission counts at different emission peaks and the time scale of the successive energy transfer is clear from Figure 4 f. The peak intensity at 555 nm reached a maximum within 0.19 ns followed by decay, whereas the 600 nm emission reached its maximum at 0.41 ns. The rise time value (0.97 ns) obtained at 600 nm can be correlated with the decay component (0.81 ns) observed at 555 nm. In a similar fashion, 650 and 725 nm peak reached their maximum within 0.49 and 0.56 ns, respectively and then decayed. A negative pre-exponential factor observed at 650 and 725 nm emission decays confirms the stepwise energy transfer from 555 to 600 nm, 600 to 650 nm, 650 to 725 nm and then a weak energy transfer from the 725 to 790 nm, suggesting multiple long-range cascade energy transfer.^[6a,16b,c,20d,e] The BODIPY **2**, albeit having a chiral side chain, did not show any supramolecular chirality and exhibited the same behavior as of **1** with respect to the optical and morphological properties (Figures S11–S13).

Further insights on the cascade energy transfer could be obtained from time-resolved anisotropy studies (Figure 4 g-i). In general, the loss of anisotropy of organized donors within an assembly occurs either through rotational motion or energy migration.^[16,30] In n-decane, depolarization through rotational motion is less favored as spontaneous nucleation assists the formation of 2D assemblies and hence energy migration can be the possible pathway for depolarization.^[16,30] At 3×10^{-4} M, 1 in *n*-decane exhibited an initial anisotropy value (r_0) of 0.25 and reached the plateau region (r_∞) at 0.13 by losing the anisotropy with a decay time, $\tau_r = 45$ ps (Figure 4h). The r_0 value of 0.25 at around zero time indicates that the initial orientation of the transition dipole moments has an angle of 30°.^[31] On the other hand, at a similar concentration in MCH, the initial anisotropy (r_0) was found to be 0.15, which reached the final anisotropy (r_{∞}) value of -0.04 (Figure 4g). The difference in the initial anisotropy value indicates the random independent orientation of the chromophores in MCH, where a large angle (40°) exists between the excitation and emission dipole moments. Interestingly, the studies carried out in *n*-decane after sonication showed a higher initial anisotropy (r_0) value of 0.32, where the angle (21°)



Figure 4. Time-resolved emission (TRES) of 1 in a) MCH, b) *n*-decane before sonication and c) after sonication. The normalized fluorescence decay curves in d) MCH, e) *n*-decane before sonication and f) after sonication; monitored at different emission wavelengths $(3 \times 10^{-4} \text{ M}, \lambda_{ex} = 375 \text{ nm})$. Time-resolved fluorescence anisotropy decay in g) MCH ($\lambda_{em} = 550 \text{ nm}$), h) *n*-decane ($\lambda_{em} = 555 \text{ nm}$) before sonication and i) after sonication ($3 \times 10^{-4} \text{ M}, \lambda_{ex} = 375 \text{ nm}$).

between the excitation and emission transition dipole moments was found to be much smaller in comparison to the other cases (Figure 4i). In addition, the final anisotropy (r_{∞}) value of 0.04 was reached within a short decay time (τ_r) of 28 ps. The anisotropy decay time τ_r , which gives an estimation of the rate of energy migration $(k_{\rm EM})$ from the higher to the lower energy state,^[16b,c] was found to be 3.57×10^{10} and $2.22 \times 10^{10} \, {\rm s}^{-1}$ for sonicated and non-sonicated samples, respectively. The fast fluorescence depolarization and energy migration rate obtained in sonicated *n*-decane sample signify a fast interchromophore energy migration of a singlet exciton,^[16,30] facilitating successive and partial energy transfer process within the aggregates having different HOMO–LUMO energy levels.

The solvent dependent origin of the distinct morphological features and the associated excited state property could be rationalized based on the difference in molecular packing (Figure 5) as evident from various experimental results. The antiparallel arrangement of the dipoles can lead to a centrosymmetric dimer structure,^[32] as inferred from the *d*-spacing value of 56.2 Å obtained from the wide-angle X-ray scattering (Figure S14). These centrosymmetric dimers can further involve in the nucleation process dictated by the nature of the solvent molecules (Figure 5).^[27] In the case of MCH, the nucleation process was sluggish ($T_e = 321$ K) in comparison to that in *n*-decane ($T_e = 358$ K) due to the difference in the activation energy barriers (Figure 5). The fast nucleationelongation process in n-decane resulted in 2D sheets stabilized by intermolecular H-bonding and interdigitated alkyl chains. Fourier transform-infrared (FT-IR) studies have shown that the 2D sheets formed in *n*-decane are stabilized by various non-covalent interactions (Figure S15). Film state FT-IR spectrum of 1 obtained from *n*-decane exhibited bands at 3288, 1640 and 1545 cm⁻¹, suggesting intermolecular Hbonding.^[12b,21a] On the other hand, the BODIPY 1 in CDCl₃ displayed two bands at 3450 and 3348 cm⁻¹, assigned as amide A bands. The amide I and II bands appeared at 1654 and 1543 cm⁻¹, respectively. Intramolecular H-bonding was overruled based on the negligible hysteresis observed between cooling and heating curves for the n-decane aggregates and also from the identical cooling curves obtained when the cooling rate was varied from 1 to 5 $\mathrm{K} \mathrm{min}^{-1}$ (Figure S16). In addition, the symmetric and asymmetric -CH₂ vibrations of **1** in the xerogel state were observed at 2852 and 2922 cm^{-1} ,



Figure 5. Schematic energy landscape diagram for the morphology dependent exciton deactivation in BODIPY assemblies. Self-assembly in MCH (left panel, pathway A) and *n*-decane (right panel, pathway B), forming spherical supramolecular structures and 2D sheets, leading to normal (single emission) and cascade energy transfer, respectively.

respectively and shifted towards the lower frequency region with respect to 1 in CDCl₃ (Figure S17a), indicating that the dodecyl chains of 1 remain in all trans configuration and interdigitated in the 2D assembly forming aggregates.^[12b] These sheets possess anisotropically organized aggregates of BODIPY chromophores with different energy band gaps leading to multi-emissive feature. In addition, the sluggish nucleation-elongation of 1 in MCH resulted in small particles (upon fast cooling) and their subsequent coalescence to large spheres with time, forming isotropically organized assembly of the BODIPY chromophores leading to a single emission peak. In this case, amide A, I and II bands were observed at 3289, 1637 and 1506 cm⁻¹, respectively, suggesting the formation of intermolecular H-bonding between the molecules (Figure S15 and S16). However, FT-IR bands corresponding to symmetric and asymmetric -CH₂ vibrations were almost indistinguishable in the case of 1 in MCH and CDCl₃, indicating randomly arranged dodecyl chains and thus unable to form gels (Figure S17b). The self-assembly of BODIPY derivative **3** having short butyl chains in *n*-decane $(3 \times 10^{-4} \text{ M})$ resulted in a single emission maximum at 527 nm upon excitation at 475 nm (Figure S18a). Furthermore, failure of 3 to form a gel in *n*-decane $(8 \times 10^{-3} \text{ M})$ and instead of forming spherical particle-like precipitates (Figure S18b) underpin the role of long hydrocarbon side chains in the observed 2D morphology of 1 and 2 in *n*-decane.

Conclusion

The spherical morphology formed through the multistep assembly of the BODIPY 1 in MCH behaves like a normal chromophore assembly in terms of the excited state behavior; however, the 2D sheets formed in n-decane exhibits an unusual multi-emission associated with successive energy transfer within the energetically anisotropic chromophore assembly landscape. The long hydrocarbon chains in 1 and 2 are essential for forming 2D sheets, as illustrated with the inability of 3 to form such assembly in linear non-polar solvents. The transformation between the spherical assembly in MCH and 2D sheets in *n*-decane along with the changes from single to multiple emission underpin an assemblydependent excited state behavior. Our results show that it is possible to reversibly control the excited state properties with two different stimuli such as solvent composition and ultrasound. Moreover, the effect of ultrasound stimulation of the 2D sheets on successive energy transfer with one of the largest observed pseudo Stokes-shift of 7105 cm⁻¹ may be useful for designing self-assembly based light-harvesting and photonic devices. Though there are many reports on cascade energy transfer, the present system is the only example available on intentionally modulated cascade energy transfer in a chromophore based supramolecular system, which can be reversibly controlled with solvents as a consequence of morphological change.

Acknowledgements

A.A. is grateful to the DST-SERB, Govt. of India, for a J. C. Bose National Fellowship (SB/S2/JCB-11/2014). G.D. and A.P. acknowledges CSIR and UGC, Govt. of India for research fellowships, respectively. We acknowledge Dr. B. Vedhanarayanan and Dr. V. Karunakaran (CSIR-NIIST) for their support and scientific discussion at different stages of this work. We thank Kiran Mohan and Harish Raj V. (CSIR-NIIST) for TEM and SEM measurements, respectively.

Conflict of interest

The authors declare no conflict of interest.

Keywords: BODIPY \cdot fluorescence \cdot organic dye \cdot self-assembly \cdot supramolecular polymer

- a) H. W. Schmidt, F. Würthner, Angew. Chem. Int. Ed. 2020, 59, 8766–8775; Angew. Chem. 2020, 132, 8846–8856; b) G. Vantomme, E. W. Meijer, Science 2019, 363, 1396–1397; c) M. Aono, Y. Bando, K. Ariga, Adv. Mater. 2012, 24, 150–151.
- [2] a) H. Zhang, Z. Zhao, A. T. Turley, L. Wang, P. R. McGonigal, Y. Tu, Y. Li, Z. Wang, R. T. K. Kwok, J. W. Y. Lam, et al., *Adv. Mater.* 2020, *32*, 2001457; b) V. K. Praveen, B. Vedhanarayanan, A. Mal, R. K. Mishra, A. Ajayaghosh, *Acc. Chem. Res.* 2020, *53*, 496–507; c) S. Varughese, *J. Mater. Chem. C* 2014, *2*, 3499–3516; d) L. Maggini, D. Bonifazi, *Chem. Soc. Rev.* 2012, *41*, 211–241.
- [3] a) P. K. Hashim, J. Bergueiro, E. W. Meijer, T. Aida, Prog. Polym. Sci. 2020, 105, 101250; b) R. D. Mukhopadhyay, A. Ajayaghosh, Science 2015, 349, 241-242.
- [4] a) B. Shen, Y. Kim, M. Lee, Adv. Mater. 2020, 32, 1905669; b) K. Ariga, S. Watanabe, T. Mori, J. Takeya, NPG Asia Mater. 2018, 10, 90–106; c) F. Ishiwari, Y. Shoji, T. Fukushima, Chem. Sci. 2018, 9, 2028–2041.
- [5] a) M. Wehner, F. Würthner, *Nat. Rev. Chem.* **2020**, *4*, 38–53; b) J. Matern, Y. Dorca, L. Sánchez, G. Fernández, *Angew. Chem. Int. Ed.* **2019**, *58*, 16730–16740; *Angew. Chem.* **2019**, *131*, 16884–16895; c) A. Sorrenti, J. Leira-Iglesias, A. J. Markvoort, T. F. A. de Greef, T. M. Hermans, *Chem. Soc. Rev.* **2017**, *46*, 5476–5490.
- [6] a) X. Jin, M. B. Price, J. R. Finnegan, C. E. Boott, J. M. Richter, A. Rao, S. M. Menke, R. H. Friend, G. R. Whittell, I. Manners, *Science* 2018, 360, 897–900; b) Z. M. Hudson, D. J. Lunn, M. A. Winnik, I. Manners, *Nat. Commun.* 2014, 5, 3372.
- [7] a) A. Sarkar, T. Behera, R. Sasmal, R. Capelli, C. Empereurmot, J. Mahato, S. S. Agasti, G. M. Pavan, A. Chowdhury, S. J. George, J. Am. Chem. Soc. 2020, 142, 11528–11539; b) W. Wagner, M. Wehner, V. Stepanenko, S. Ogi, F. Würthner, Angew. Chem. Int. Ed. 2017, 56, 16008–16012; Angew. Chem. 2017, 129, 16224–16228; c) S. Ogi, K. Sugiyasu, S. Manna, S. Samitsu, M. Takeuchi, Nat. Chem. 2014, 6, 188–195.
- [8] a) B. Adhikari, Y. Yamada, M. Yamauchi, K. Wakita, X. Lin, K. Aratsu, T. Ohba, T. Karatsu, M. J. Hollamby, N. Shimizu, et al., *Nat. Commun.* 2017, *8*, 15254; b) A. Gopal, M. Hifsudheen, S. Furumi, M. Takeuchi, A. Ajayaghosh, *Angew. Chem. Int. Ed.* 2012, *51*, 10505–10509; *Angew. Chem.* 2012, *124*, 10657–10661.
- [9] a) G. Panzarasa, A. L. Torzynski, T. Sai, K. Smith-Mannschott, E. R. Dufresne, *Soft Matter* **2020**, *16*, 591–594; b) H. A. M. Ardoña, E. R. Draper, F. Citossi, M. Wallace, L. C. Serpell, D. J. Adams, J. D. Tovar, *J. Am. Chem. Soc.* **2017**, *139*, 8685–8692.
- [10] a) T. K. Ellis, M. Galerne, J. J. Armao, A. Osypenko, D. Martel, M. Maaloum, G. Fuks, O. Gavat, E. Moulin, N. Giuseppone, *Angew. Chem. Int. Ed.* 2018, *57*, 15749–15753; *Angew. Chem.*

2018, *130*, 15975–15979; b) J. Leira-Iglesias, A. Tassoni, T. Adachi, M. Stich, T. M. Hermans, *Nat. Nanotechnol.* **2018**, *13*, 1021–1027.

- [11] a) H. He, W. Tan, J. Guo, M. Yi, A. N. Shy, B. Xu, *Chem. Rev.* 2020, *120*, 9994–10078; b) M. Kumar, N. L. Ing, V. Narang, N. K. Wijerathne, A. I. Hochbaum, R. V. Ulijn, *Nat. Chem.* 2018, *10*, 696–703.
- [12] a) X. Yu, L. Chen, M. Zhang, T. Yi, *Chem. Soc. Rev.* 2014, *43*, 5346–5371; b) J. M. Malicka, A. Sandeep, F. Monti, E. Bandini, M. Gazzano, C. Ranjith, V. K. Praveen, A. Ajayaghosh, N. Armaroli, *Chem. Eur. J.* 2013, *19*, 12991–13001; c) N. Komiya, T. Muraoka, M. Iida, M. Miyanaga, K. Takahashi, T. Naota, *J. Am. Chem. Soc.* 2011, *133*, 16054–16061.
- [13] a) P. Xing, Y. Li, Y. Wang, P.-Z. Li, H. Chen, S. Z. F. Phua, Y. Zhao, *Angew. Chem. Int. Ed.* **2018**, *57*, 7774–7779; *Angew. Chem.* **2018**, *130*, 7900–7905; b) K. V. Rao, D. Miyajima, A. Nihonyanagi, T. Aida, *Nat. Chem.* **2017**, *9*, 1133–1139.
- [14] a) A. Mishra, S. Dhiman, S. J. George, Angew. Chem. Int. Ed.
 2021, 60, 2740-2756; Angew. Chem. 2021, 133, 2772-2788; b) B.
 Rieß, R. K. Grötsch, J. Boekhoven, Chem 2020, 6, 552-578.
- [15] a) N. Adir, S. Bar-Zvi, D. Harris, *Biochim. Biophys. Acta Bioenerg.* 2020, 1861, 148047; b) T. Brixner, R. Hildner, J. Köhler, C. Lambert, F. Würthner, Adv. Energy Mater. 2017, 7, 1700236; c) K.-T. Wong, D. M. Bassani, NPG Asia Mater. 2014, 6, e116; d) V. K. Praveen, C. Ranjith, N. Armaroli, Angew. Chem. Int. Ed. 2014, 53, 365 368; Angew. Chem. 2014, 126, 373 376; e) Structure and Function of Phycobilisomes, M. Mimuro, H. Kikuchi, A. Murakami in Concepts in Photobiology: Photosynthesis and Photomorphogenesis, (Eds.: G. S. Singhal, G. Rengel, S. K. Sopory, K.-D. Irrgang, Govindjee), Narosa Publishing House, New Delhi, 1999.
- [16] a) C. Giansante, C. Schäfer, G. Raffy, A. Del Guerzo, J. Phys. Chem. C 2012, 116, 21706–21716; b) C. Vijayakumar, V. K. Praveen, A. Ajayaghosh, Adv. Mater. 2009, 21, 2059–2063; c) A. Ajayaghosh, V. K. Praveen, C. Vijayakumar, S. J. George, Angew. Chem. Int. Ed. 2007, 46, 6260–6265; Angew. Chem. 2007, 119, 6376–6381.
- [17] a) J. Bañuelos, Chem. Rec. 2016, 16, 335-348; b) G. Ulrich, R. Ziessel, A. Harriman, Angew. Chem. Int. Ed. 2008, 47, 1184-1201; Angew. Chem. 2008, 120, 1202-1219; c) A. Loudet, K. Burgess, Chem. Rev. 2007, 107, 4891-4932.
- [18] a) Z. Liu, Z. Jiang, M. Yan, X. Wang, *Front. Chem.* 2019, 7, 712;
 b) A. V. Solomonov, Y. S. Marfin, E. V. Rumyantsev, *Dyes Pigm.* 2019, *162*, 517–542; c) S. Cherumukkil, B. Vedhanarayanan, G. Das, V. K. Praveen, A. Ajayaghosh, *Bull. Chem. Soc. Jpn.* 2018, *91*, 100–120.
- [19] a) I. Helmers, G. Ghosh, R. Q. Albuquerque, G. Fernández, Angew. Chem. Int. Ed. 2021, 60, 4368-4376; Angew. Chem.
 2021, 133, 4414-4423; b) I. Helmers, B. Shen, K. K. Kartha, R. Q. Albuquerque, M. Lee, G. Fernández, Angew. Chem. Int. Ed. 2020, 59, 5675-5682; Angew. Chem. 2020, 132, 5724-5731; c) I. Helmers, N. Bäumer, G. Fernández, Chem. Commun. 2020, 56, 13808-13811; d) I. Helmers, M. Niehues, K. K. Kartha, B. J. Ravoo, G. Fernández, Chem. Commun. 2020, 56, 8944-8947; e) J. Xia, E. Busby, S. N. Sanders, C. Tung, A. Cacciuto, M. Y. Sfeir, L. M. Campos, ACS Nano 2017, 11, 4593-4598; f) S. Cherumukkil, S. Ghosh, V. K. Praveen, A. Ajayaghosh, Chem. Sci. 2017, 8, 5644-5649; g) J.-H. Olivier, J. Widmaier, R. Ziessel, Chem. Eur. J. 2011, 17, 11709-11714.
- [20] a) S. Radunz, W. Kraus, F. A. Bischoff, F. Emmerling, H. R. Tschiche, U. Resch-Genger, *J. Phys. Chem. A* 2020, *124*, 1787–1797; b) J. Gemen, J. Ahrens, L. J. W. Shimon, R. Klajn, *J. Am. Chem. Soc.* 2020, *142*, 17721–17729; c) Y. Zhang, P. Liu, H. Pan, H. Dai, X.-K. Ren, Z. Chen, *Chem. Commun.* 2020, *56*, 12069–12072; d) D. Tian, F. Qi, H. Ma, X. Wang, Y. Pan, R. Chen, Z. Shen, Z. Liu, L. Huang, W. Huang, *Nat. Commun.* 2018, *9*, 2688; e) D. Okada, T. Nakamura, D. Braam, T. D. Dao, S. Ishii, T.

Angewandte International Edition Chemie

Nagao, A. Lorke, T. Nabeshima, Y. Yamamoto, *ACS Nano* **2016**, *10*, 7058–7063; f) S. Kim, J. Bouffard, Y. Kim, *Chem. Eur. J.* **2015**, *21*, 17459–17465; g) N. K. Allampally, A. Florian, M. J. Mayoral, C. Rest, V. Stepanenko, G. Fernández, *Chem. Eur. J.* **2014**, *20*, 10669–10678.

- [21] a) G. Das, R. Thirumalai, B. Vedhanarayanan, V. K. Praveen, A. Ajayaghosh, *Adv. Opt. Mater.* 2020, *29*, 1703783; b) B. Adelizzi, I. A. W. Filot, A. R. A. Palmans, E. W. Meijer, *Chem. Eur. J.* 2017, *23*, 6103–6110; c) H. M. M. ten Eikelder, A. J. Markvoort, T. F. A. de Greef, P. A. J. Hilbers, *J. Phys. Chem. B* 2012, *116*, 5291–5301.
- [22] N. J. Hestand, F. C. Spano, Chem. Rev. 2018, 118, 7069-7163.
- [23] a) G. Liu, M. Cai, X. Wang, F. Zhou, W. Liu, ACS Appl. Mater. Interfaces 2014, 6, 11625–11632; b) T. M. Ruhland, P. M. Reichstein, A. P. Majewski, A. Walther, A. H. E. Müller, J. Colloid Interface Sci. 2012, 374, 45–53.
- [24] a) C. D. Jones, J. W. Steed, *Chem. Soc. Rev.* 2016, 45, 6546–6596;
 b) S. Srinivasan, S. S. Babu, V. K. Praveen, A. Ajayaghosh, *Angew. Chem. Int. Ed.* 2008, 47, 5746–5749; *Angew. Chem.* 2008, 120, 5830–5833.
- [25] a) S. Dhiman, R. Ghosh, S. Sarkar, S. J. George, *Chem. Sci.* 2020, *11*, 12701–12709; b) X. Xiao, H. Chen, X. Dong, D. Ren, Q. Deng, D. Wang, W. Tian, *Angew. Chem. Int. Ed.* 2020, *59*, 9534–9541; *Angew. Chem.* 2020, *132*, 9621–9628; c) N. Sasaki, J. Yuan, T. Fukui, M. Takeuchi, K. Sugiyasu, *Chem. Eur. J.* 2020, *26*, 7840–7846; d) S. Yang, S. Y. Kang, T. L. Choi, *J. Am. Chem. Soc.* 2019, *141*, 19138–19143; e) Y. Liu, C. Peng, W. Xiong, Y. Zhang, Y. Gong, Y. Che, J. Zhao, *Angew. Chem. Int. Ed.* 2017, *56*, 11380–11384; *Angew. Chem.* 2017, *129*, 11538–11542; f) M. E. Robinson, A. Nazemi, D. J. Lunn, D. W. Hayward, C. E. Boott, M. S. Hsiao, R. L. Harniman, S. A. Davis, G. R. Whittell, R. M. Richardson, et al., *ACS Nano* 2017, *11*, 9162–9175.
- [26] a) E. E. Greciano, J. Calbo, E. Ortí, L. Sánchez, Angew. Chem. Int. Ed. 2020, 59, 17517-17524; Angew. Chem. 2020, 132, 17670-17677; b) A. Chakraborty, G. Ghosh, D. S. Pal, S. Varghese, S. Ghosh, Chem. Sci. 2019, 10, 7345-7351; c) Y. Lin, M. Penna, M. R. Thomas, J. P. Wojciechowski, V. Leonardo, Y. Wang, E. T.

Pashuck, I. Yarovsky, M. M. Stevens, *ACS Nano* **2019**, *13*, 1900–1909; d) M. Pfeffermann, R. Dong, R. Graf, W. Zajaczkowski, T. Gorelik, W. Pisula, A. Narita, K. Müllen, X. Feng, *J. Am. Chem. Soc.* **2015**, *137*, 14525–14532; e) M. Vybornyi, A. V. Rudnev, S. M. Langenegger, T. Wandlowski, G. Calzaferri, R. Häner, *Angew. Chem. Int. Ed.* **2013**, *52*, 11488–11493; *Angew. Chem.* **2013**, *125*, 11702–11707.

- [27] a) M. F. J. Mabesoone, A. R. A. Palmans, E. W. Meijer, J. Am. Chem. Soc. 2020, 142, 19781–19798; b) G. Ghosh, S. Ghosh, Chem. Commun. 2018, 54, 5720–5723; c) C. Kulkarni, P. A. Korevaar, K. K. Bejagam, A. R. A. Palmans, E. W. Meijer, S. J. George, J. Am. Chem. Soc. 2017, 139, 13867–13875; d) K. Baek, I. Hwang, I. Roy, D. Shetty, K. Kim, Acc. Chem. Res. 2015, 48, 2221–2229; e) Q. Jin, L. Zhang, M. Liu, Chem. Eur. J. 2013, 19, 9234–9241.
- [28] B. Wittmann, F. A. Wenzel, S. Wiesneth, A. T. Haedler, M. Drechsler, K. Kreger, J. Köhler, E. W. Meijer, H.-W. Schmidt, R. Hildner, J. Am. Chem. Soc. 2020, 142, 8323–8330.
- [29] Emission properties of the BODIPY has been reported to be controlled in mixed lipid monolayers by molecular compression at the air-water interface. T. Mori, H. Chin, K. Kawashima, H. T. Ngo, N. J. Cho, W. Nakanishi, J. P. Hill, K. Ariga, ACS Nano 2019, 13, 2410-2419.
- [30] P. C. Nandajan, H. J. Kim, S. Casado, S. Y. Park, J. Gierschner, J. Phys. Chem. Lett. 2018, 9, 3870–3877.
- [31] A. U. Neelambra, C. Govind, T. T. Devassia, G. M. Somashekharappa, V. Karunakaran, *Phys. Chem. Chem. Phys.* 2019, 21, 11087-11102.
- [32] a) C. Kulkarni, S. Balasubramanian, S. J. George, *ChemPhys-Chem* 2013, 14, 661-673; b) F. Würthner, S. Yao, U. Beginn, *Angew. Chem. Int. Ed.* 2003, 42, 3247-3250; *Angew. Chem.* 2003, 115, 3368-3371.

Manuscript received: November 18, 2020 Accepted manuscript online: January 11, 2021 Version of record online: March 3, 2021