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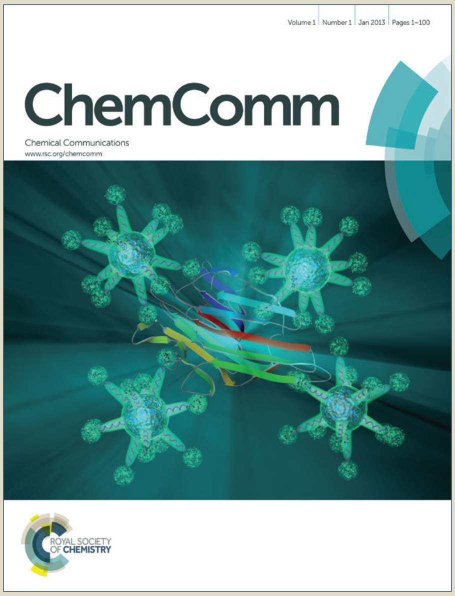

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Tunable light emission from co-assembled structures of benzothiadiazole molecules

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Co-assembled structures possessing tunable light emission from 510–690 nm have been prepared using various compositions of two different 4,7-substituted benzothiadiazole molecules, 1 and 2. The preferential incorporation and co-localization of 1 with 2 to produce co-assemblies is possible because of structural similarities and allows for tuning of morphology and light emission.

Controlling morphology to impact optical and electrical properties in functional self-assembled organic materials has been a key focus of research in recent times.[1] Although considerable progress has been made in utilizing individual molecular entities to produce desired self-assembled structures, it has been challenging to address morphological control beyond individual components towards yielding functionally rich co-assembled structures.[2] Shish-kabab[2a] like structures that have high photovoltages[2c] has been reported for P3HT-PDI combinations along with epitaxial grown binary structures[2b] for advance photonic and opto-electronic applications. Such complex self-assembly indicates the intricate nature of molecular interactions that allow for such strategic molecular combinations while maintaining unique morphologies. In the aforementioned cases with complex self-assembled structures, there is considerable disparity in the size of the two distinct entities leading to phase separated yet side-by-side shish-kabab or hetero structure assembly.[2a-c] Also, bimolecular co-assemblies capable of showing energy transfer (FRET) has been explored.[2e] An interesting scenario that remains unexplored thus far relates to the possibility of co-localizing two-distinct molecular entities in close proximity yet maintaining sufficient molecular features to allow light emission.[3] Aggregated induced emission (AIE) has been observed in molecular systems where there is considerable distortion in the geometrical features.[4] While AIE has been observed in individual organic molecular assemblies, a major challenge that remains sparsely explored is the ability to prepare fluorescent co-assembled structures comprised of two distinct molecular entities for enabling tailored light emission from compositionally controlled co-assembled structures. While such tunable light emission is possible in inorganic quantum dots by virtue of their size,[5] in organic materials co-localization of molecular entities could lead to new possibilities towards controlling both optical and electrical characteristics. In this article, we describe several polymorphs from two distinct individual molecular structures based on 4,7-substituted-2,1,3-benzothiadiazole molecules (BTD) **1** and **2** (**Fig. 1A-B**), followed by co-assemblies resulting from favourable composition control of the two molecular components. Furthermore, the co-localization of the two molecular entities within the co-assembled structure shows tunable light emission characteristics. Such composition controlled co-assembled structures have not yet been realized for functional π-class of electron acceptors based on BTD and enables realm of possibilities in opto-electronics and photonics.

The molecules **1** and **2**, belonging to BTD family, possess unique optical and electrical characteristics, and have been exploited in a range of opto-electronic applications because of properties such as high absorptivities and high emission quantum yields.[6] The optical absorption and emission characteristics of BTD molecules are directly influenced by the functional moieties attached to the BTD cores; in turn this has allowed for the synthesis of distinct dyes capable of light absorption and emission from ultra-violet (UV) to visible to near infrared.[6] We have recently reported ultra-long microtubules self-assembled structures from **1** that show strong light emission along with multimodal light guiding properties[1d] and polarized emission.[6e] By modifying the solution processing method, herein, we show new possibilities for realizing co-assembled structures by composition control. **1** and **2** were strategically chosen to achieve co-assemblies because of the notable strong emission from their individual assemblies along with being unique in the spectral features of the two components allowing identification of individual entities within the co-assemblies – enabling direct probing of co-localization within the co-assembled structures.

Self-assembly of pure components and compositionally mixed **1** and **2** were carried out by slow cooling of various compositions in chloroform/ethanol solutions (see experimental section, ESI†). For the composition control, five different concentrations containing varying amounts of **1** and **2**, beyond pure components of **1** and **2**, were chosen as **C2: $1_{90\%} + 2_{10\%}$, C3: $1_{75\%} + 2_{25\%}$., C4: $1_{50\%} + 2_{50\%}$, C5: $1_{25\%} + 2_{75\%}$, C6: $1_{10\%} + 2_{90\%}$,** and processed in a similar manner as described for **1** and **2**. This allows direct comparison of the morphologies and optical properties from the various compositions. **C1** and **C7** represent the two pure components **1** and **2**, respectively. The total concentration of mixture is set to 33 μM. The solutions with different compositions (**C1-C7**) are shown in **Fig. S1,** ESI†. For most of the attempted methods (with various solvents) we note that there is considerable phase separation of the components and therefore does not allow for co-assembled structures. This is caused by the incompatibility of the components in the different solvent system owing to differences in solubilities which lead to phase-separation of the components. It was found that slow cooling from ~90:10 (v/v) ethanol:chloroform solution produced well-defined morphology with uniform distribution of the two components without any phase-separation. The resulting morphologies for the various compositions (**C1-C7**) characterized by scanning electron microscopy (SEM) are shown in (**Fig. 1C-1I and Fig. S2, S4-S9,** ESI†).

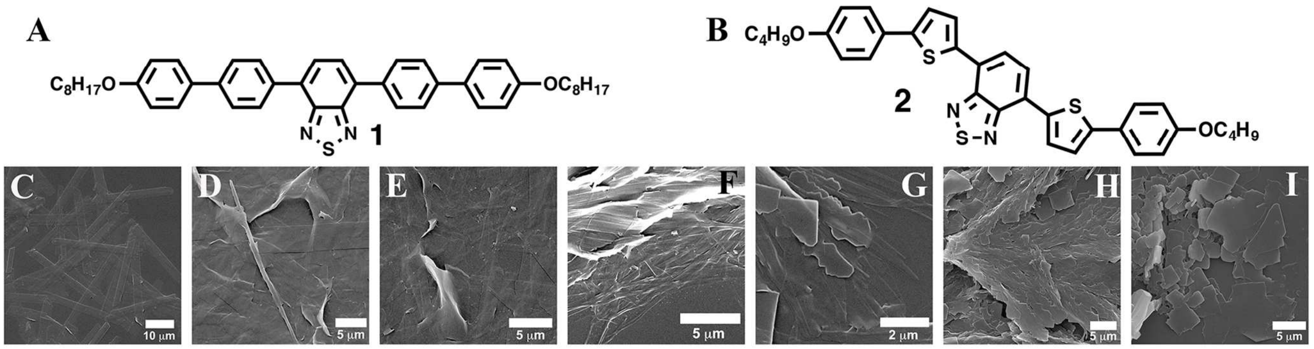

Fig. 1. **(A,B)** Chemical structures of the two BTD molecules utilized for achieving co-assembled structures. **(C-I)** Scanning electron microscopy images for the resulting morphology of **C1-C7** using chloroform: ethanol mixtures.

Pure **1** produces micro-ribbon like morphology (**Fig. 1C** and **Fig. S2**, ESI†) upon slow cooling from ethanol/chloroform mixture, while extremely large microtubules were produced for **1** by phase-transfer in methanol.[1d] Such morphology change indicates the subtle interplay of different packing interactions, dictated by the local geometry, amongst the molecules of **1**. Polymorphs are not uncommon in π-functional molecules considering the constraints of optimized geometries in molecular entities particularly when conditions of assemblies carried out in different solvents.[7] For **1**, we have previously noted that there is considerable distortion within the molecule, yet the planarity of molecule is maintained when considered from end-to-end phenyl groups (**Fig. S3**, ESI†). Such planarity of the molecule promotes weaker π-stacking among molecules and enables realization of emissive assemblies.[1d] For **2**, two distinct polymorphs are formed - 3D micro-crystallite like structures along with 2D sheet like morphology (extended ribbon like structures) can be noted (**Fig. 1I**, and **Fig. S4**, ESI†). It is interesting to note that despite considerable distortion and non-planarity of **2** (see **Fig. S3**, ESI†) well-defined morphologies can be realized. The 2D sheet and 3D crystallites are indicative of flip-flop molecular stacking likely promoted by alkyl-chain interdigitations.[8] Such interactions therefore allow exploration of new properties arising from strategic combinations of the two pure components to produce co-assembled structures. The resulting morphology from the various compositions (**C2-C6**) is shown in **Fig. 1D-1H** and **Fig. S5-S9** (ESI†). With the increase in concentration of **2** the morphology favours adoption of 2D sheet like form from 1D ribbons, presumably because of the geometric preference of **2**. This morphological change is already notable for small additions of **2** to **1**. When 10% of **2** is added to 90% **1**, there is already a considerable change in the behaviour of the aggregated structure and the widths of the co-assembled structures appear to be smaller than those of pure **1** (**Fig. 1D**, and **Fig. S5**, ESI†). As composition of **2** increases from **C2-C4**, the morphology evolves into extended ribbons with random shaped endings as noted for assemblies of pure **1** (**Fig. S5-S7**, ESI†). Eventually, for compositions **C5** and **C6**, tile and sheet like structures with faceted edges and considerable similarities to pure component **2** are the more dominant morphology (**Fig. S8-S9**, ESI†). The ability of **2** to form sheet like structures along with the planarity of **1** is therefore likely to provide favorable interactions to allow the co-assembled structures with rich possibilities towards controlling opto-electronic properties.

The molecular absorption and emission spectra from **1** and **2** are shown in **Fig. S10,** ESI†. Fluorescence spectroscopic measurements from homogeneously mixed solutions reveal that the wavelength maximum does not change with composition and the emission is consistent with those of pure individual components (**Fig. 2A**). Therefore, when the various compositions **C2-C6** in chloroform solution are excited at 405 nm (for **1**) and 505 nm (for **2**) we observe emission only at 535 nm (from **1**) or 640 nm (from **2**), representative of pure individual components. Thus, in chloroform solutions the molecules **1** and **2** are non-interacting. This scenario changes dramatically upon co-assembly in chloroform/ethanol mixtures. Fluorescence spectroscopic measurements from the co-assembled structures (see **Fig. 2B and S11,** ESI†) shows composition dependent emission wavelength peak, and for each of the composition lies in between the two pure components, a systematic progression of the maximum emission wavelength is noted as the composition of **2** increases (**Fig. 2C**). The maximum emission wavelength observed for each of composition is independent of the excitation wavelength. Initial observations using UV-photoexcitation (hand held UV-light source) revealed progressive tuning of wavelength as a function of composition (**Fig. 3A-G**) implying that despite possibilities for energy transfer, and quenching of emission from non-radiative decay, the co-assembled structures enable strategic mixing of the emitted light and further corroborates the spectrally observed shifting of peak as a function of composition. This is rather uncharacteristic of such assemblies, given the alternative possibilities in the excited state. Excited state process such as Förster resonance energy transfer (FRET) can also be ruled out for the various compositions because when **1** is excited, only new emission peak in between the two components can be observed and there is no emission peak corresponding to pure emission of **2** (or **1**). This indicates that although the co-assembled structure may have the two co-localized molecules in close proximity to one another to enable FRET, the transition dipoles may not be oriented in favorable direction to allow for such an excited state process to occur. The new emission observed as a function of composition is directly influenced by the manner in which the two molecular materials are interacting with one another and requires further experimentation to delineate the exact nature of interactions and the range of packing possibilities as a function of composition. Based on the new emission resulting from the composition control, it can however be concluded that the flexibility in the geometric configuration of **1** and **2** must allow co-localization of the two molecular entities to directly influence the optical properties in such co-assembled structures.

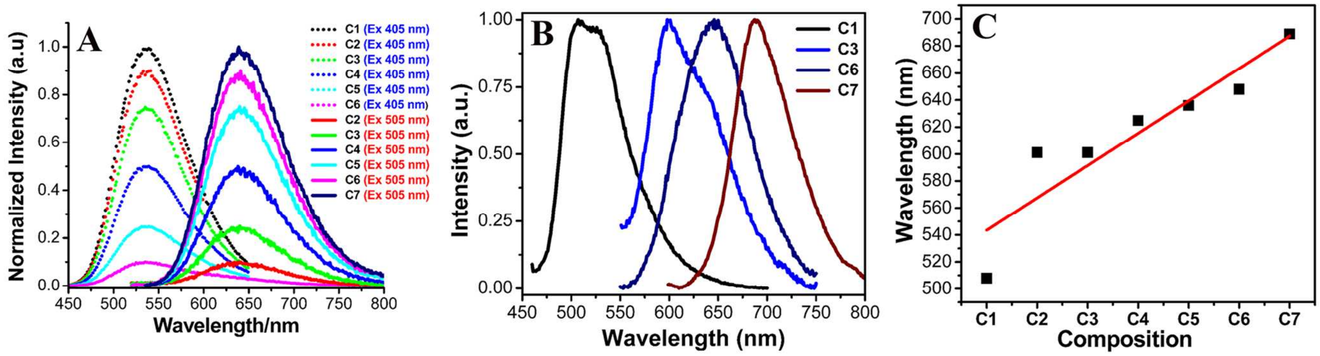

Fig. 2 **(A)** Fluorescence emission from chloroform solutions with different compositions of **1** and **2**. Depending on the excitation wavelength chosen the emission is representative of the physical mixture from individual components indicating that in solution both **1** and **2** are non-interacting. **(B)** The characteristic fluorescence emission from aggregated structures of **C1**, **C3**, **C6** and **C7**. **(C)** The progressive tuning of emission from various composition can be inferred by the plot of emission wavelength maxima for the different compositions.

The strong light emissions noted by UV-lamp excitations (**Fig.3A-G**) and bulk fluorescence measurements (**Fig. 2B** and **Fig. S11**, ESI†) on the various compositional specific co-assembled structures, however, could also be a product of two phase-separated individual - non-interacting and non-local - assemblies being present on the substrate. Fluorescence microscopy was utilized towards understanding the co-localization of the two molecular entities by observing the emission patterns from co-assembled and individual components using various available cube filters that allow for selective excitation and collecting emission in specific wavelengths. The three cube filters f1, f2 and f3 were chosen (see ESI† for more details) in such a way that emission from pure component **1** can be noted using only f1, while f2 and f3 allow for observing emission from co-assembled structures and pure **2**, respectively. **Fig. 3H-S and Fig. S12,** ESI†) shows the fluorescence microscope images from the various compositions under the different aforementioned cube filters. It can be seen that for compositions **C2-C6**, the presence of both the individual components are notable at all the regions where there is emission from the co-assembled structures. No noticeable phase separation of the two components within the co-assembled structures could be observed (**N1**, ESI†). Thus, the intricate co-localization of the two molecular entities within the co-assemblies allows for compositional control over both morphology and light emission characteristics. The co-localization of molecular entities by virtue of the geometries can therefore allow for transitions that were not possible in a tight-stacked molecular packing leading to new possibilities in opto-electronics and photonics.[3c]

In conclusion, tunable light emission from composition controlled co-assembled structures has been demonstrated because of cooperative interactions that allow for uniform co-assembled structures to be fabricated. The co-localized, co-assembled structures demonstrated here indicate the versatile combinations of the π-rich molecular groups that can be tailored to achieve strategic optical or electrical property for device applications. Future explorations are geared towards detailed characterization of fundamental structural design at molecular level for applications of such materials in the gamut of organic devices.

We acknowledge funding from the Technology Research Infrastructure Fund (TRIF). The authors received help from Prof. N. Peyghambarian's research group, and Keck instrumentation facility, UA. Special thanks to Prof. Arthur Gmitro and Mr. Mathew Rissi at UA for access and help with the fluorescence microscope.

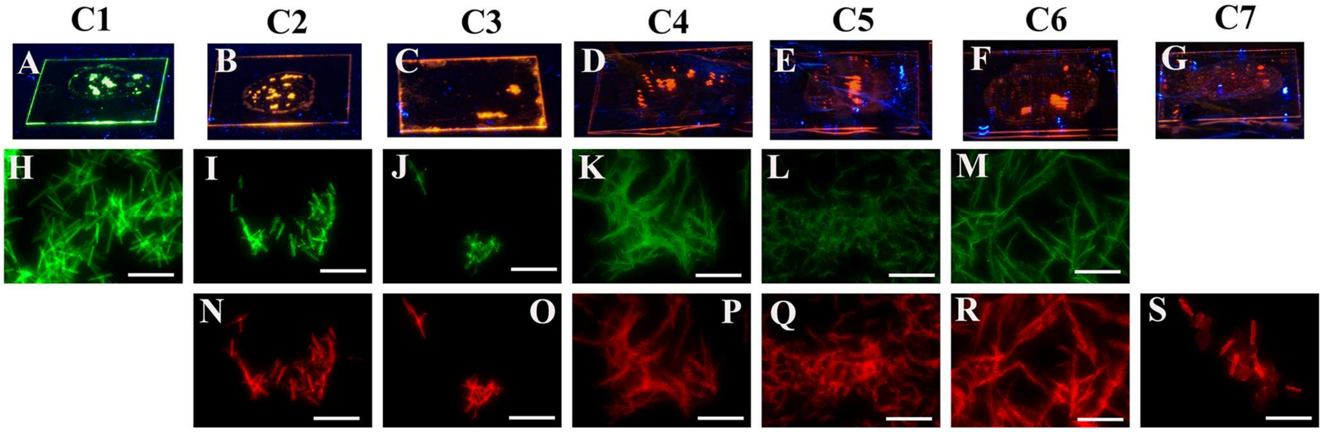

Fig. 3 (A-G) Color tunable light emission by virtue of compositional control is notable in macroscopic view by UV-photoexcitation of the pure and co-assembled structures **(H-S)** The fluorescence emissions observed for each of the compositional specific assembly under different fluorescence filter cubes indicate the co-localization of the two molecular entities within the self-assembled structures. The images **H-M** and **N-S** are obtained using **f1** and **f2** filters, respectively. The scale bar in each case is 50 μm.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, more SEM images and spectral details from individual and co-assembled structures. See DOI: 10.1039/b000000x/

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