Electronic Supplementary Material (ESI) for Chemical Science.


# Supporting Information

## "Concentration–in–Control" Self-Assembly Concept at Liquid-Solid Interface Challenged

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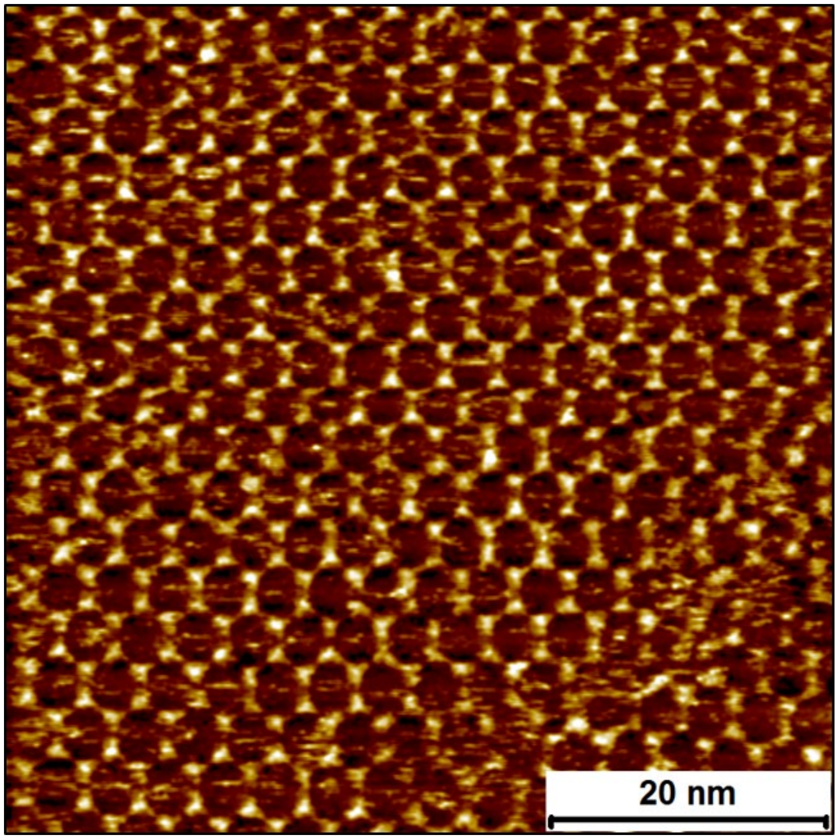


**Figure S1.** Large-scale STM image of **BT$_r$B** honeycomb porous network (**P-1**) formed at HA/HOPG interface ($C_{BTrB}$ = 4.2 × $10^{-4}$ M). Imaging parameters: $I_{set}$ = 80 pA, $V_{bias}$ = -1.0 V

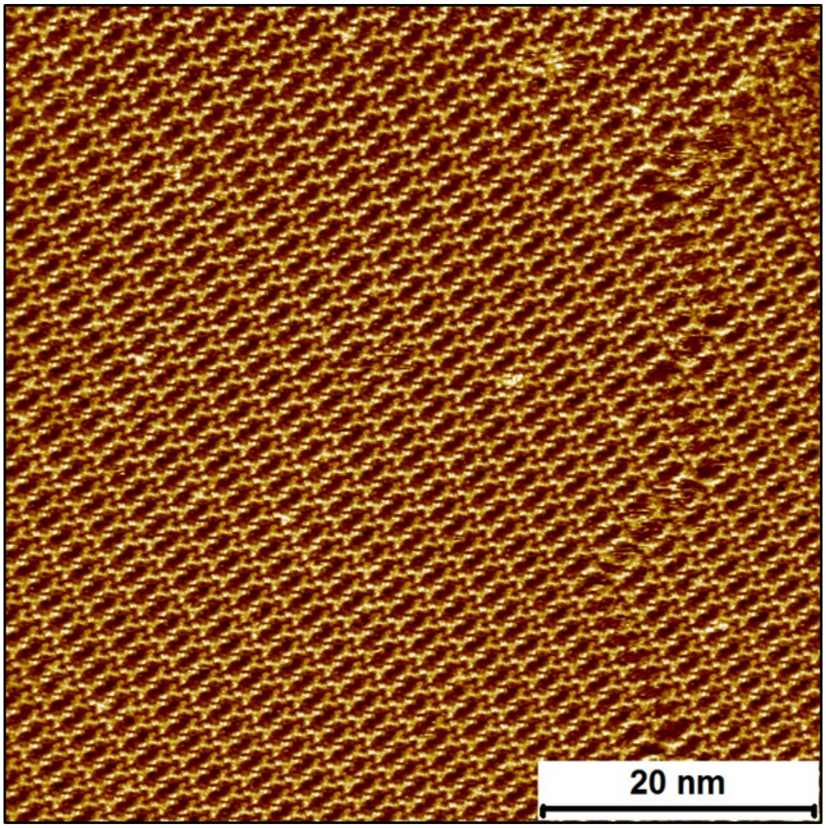


**Figure S2.** Large-scale STM image of the more compact phase of **BT$_r$B** (**P-2**) formed at HA/HOPG interface ($C_{BTrB}$ = 1.0 × $10^{-4}$ M). Imaging parameters: $I_{set}$ = 100 pA, $V_{bias}$ = -1.0 V

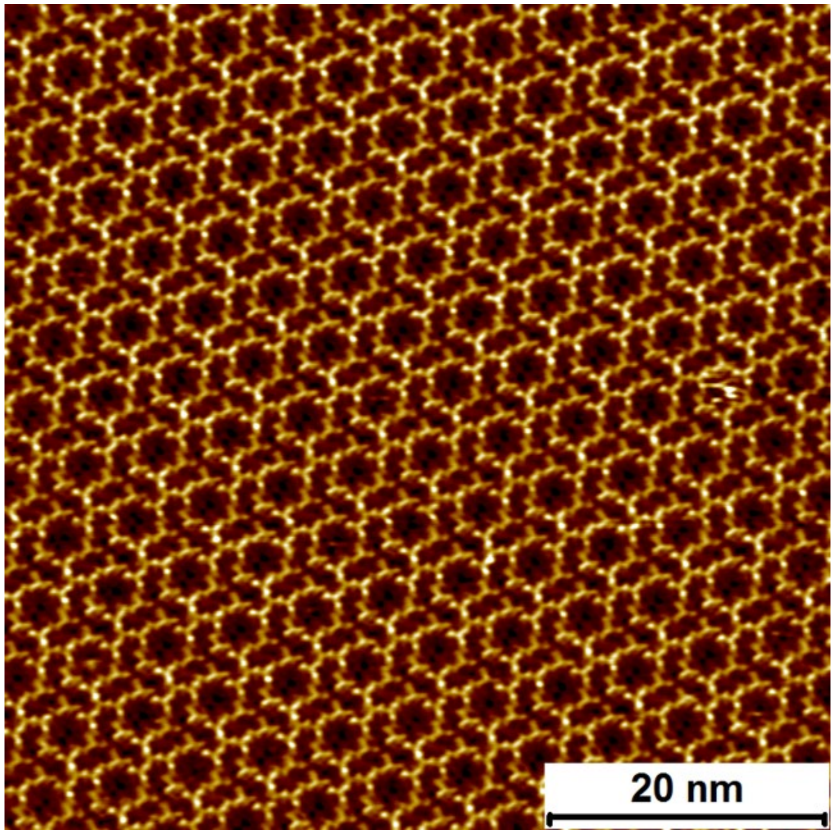


**Figure S3.** Large-scale STM image of displaced flower structure of **BT$_r$B** (**P-3**) formed at HA/HOPG interface ($C_{BTrB}$ = 1.0 × $10^{-5}$ M). Imaging parameters: $I_{set}$ = 90 pA, $V_{bias}$ = -1.0 V

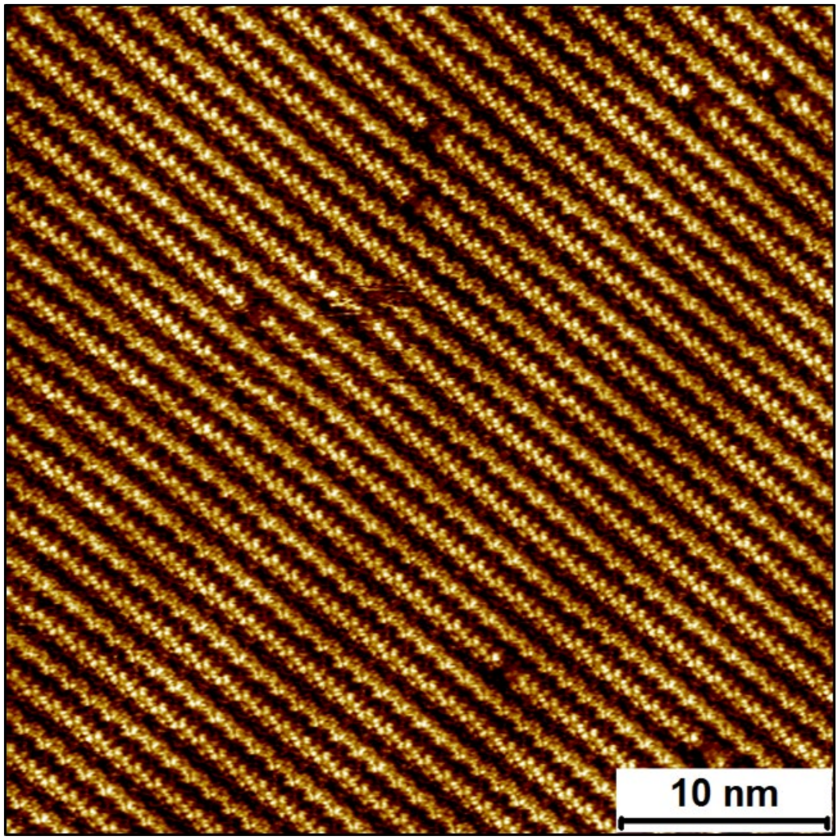


**Figure S4.** Large-scale STM image of **BTB** row structure (**P'-1**) formed at HA/HOPG interface ($C_{BTB}$ = 1.0 × $10^{-3}$ M). Imaging parameters: $I_{set}$ = 90 pA, $V_{bias}$ = -1.0 V

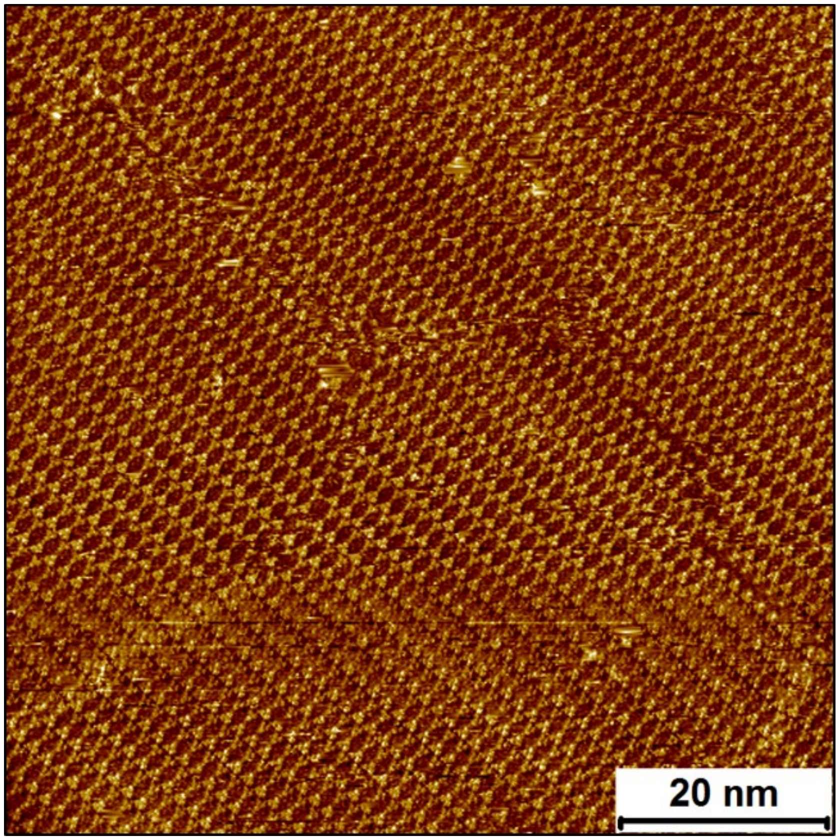


**Figure S5.** Large-scale STM image of **BTB** oblique structure (**P'-2**) formed at HA/HOPG interface ($C_{BTB}$ = 1.0 × $10^{-4}$ M). Imaging parameters: $I_{set}$ = 90 pA, $V_{bias}$ = -1.0 V

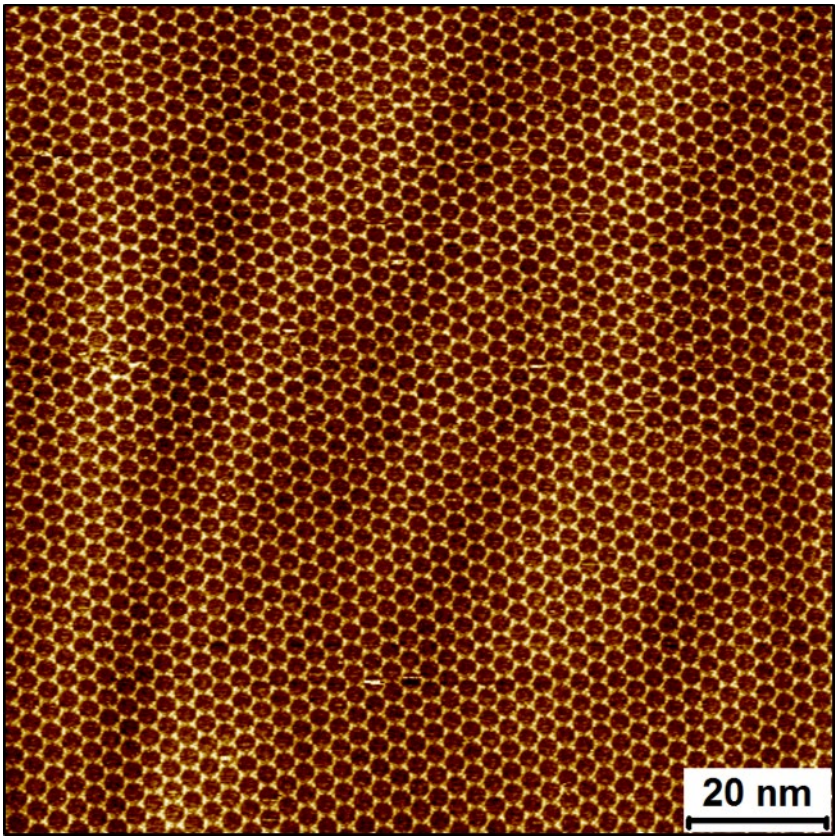


**Figure S6.** Large-scale STM image of **BTB** open porous network (**P'-3**) formed at HA/HOPG interface ($C_{BTB}$ = 3.3 × $10^{-5}$ M). Imaging parameters: $I_{set}$ = 90 pA, $V_{bias}$ = -1.0 V

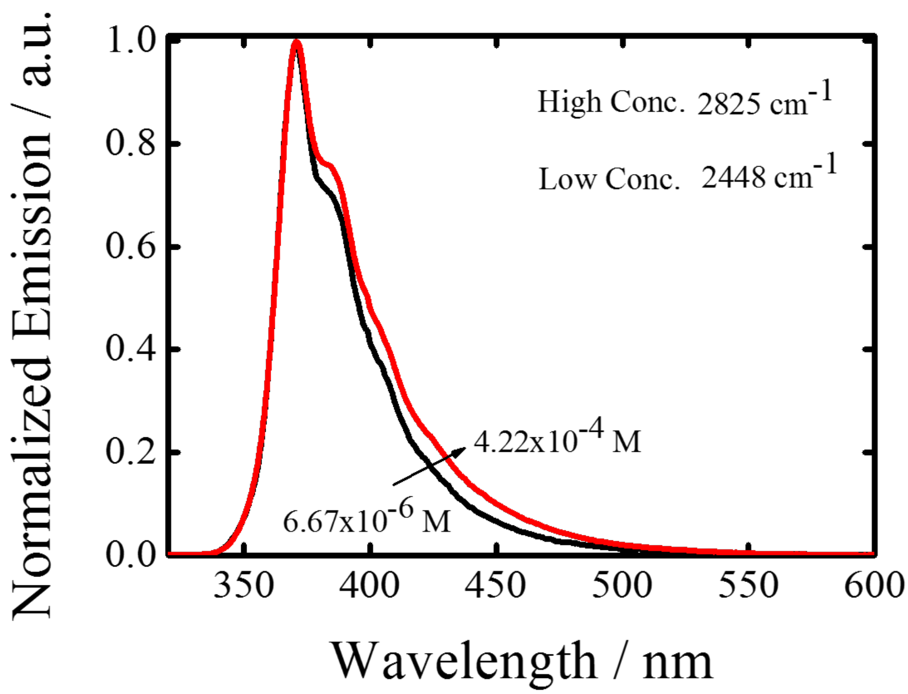


**Figure S7.** Emission spectra of **BT$_r$B** ($\lambda_{exc}$ = 320 nm) at low and high solution concentrations.

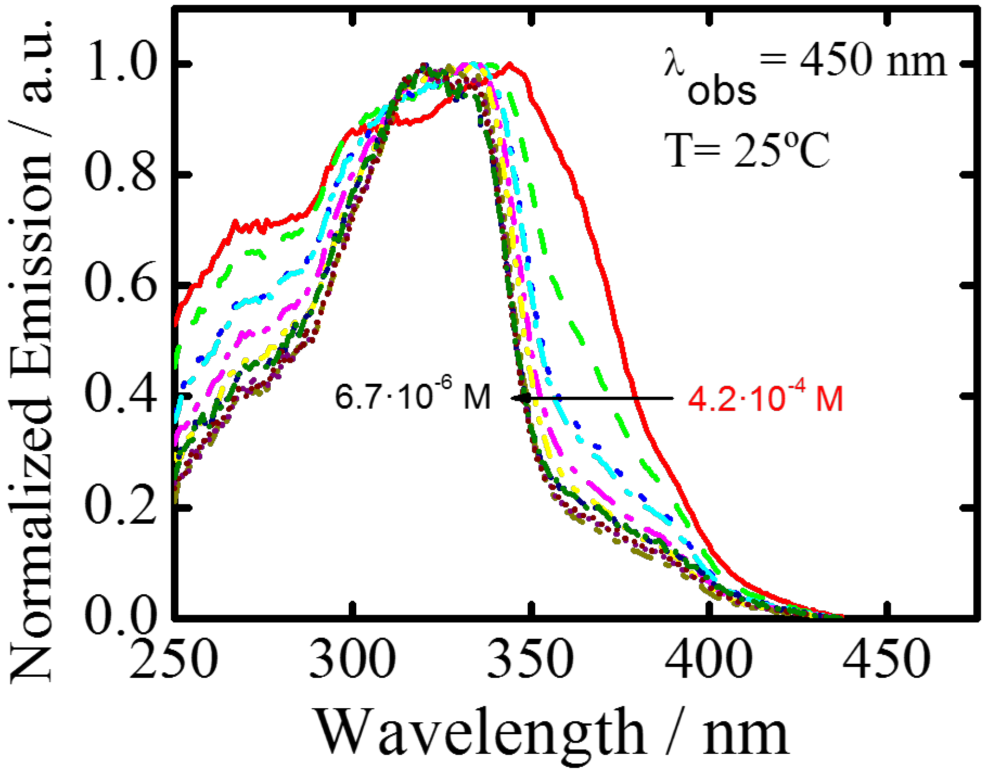


**Figure S8. Concentration dependent** excitation spectra of **BT$_r$B** at different solution concentrations.

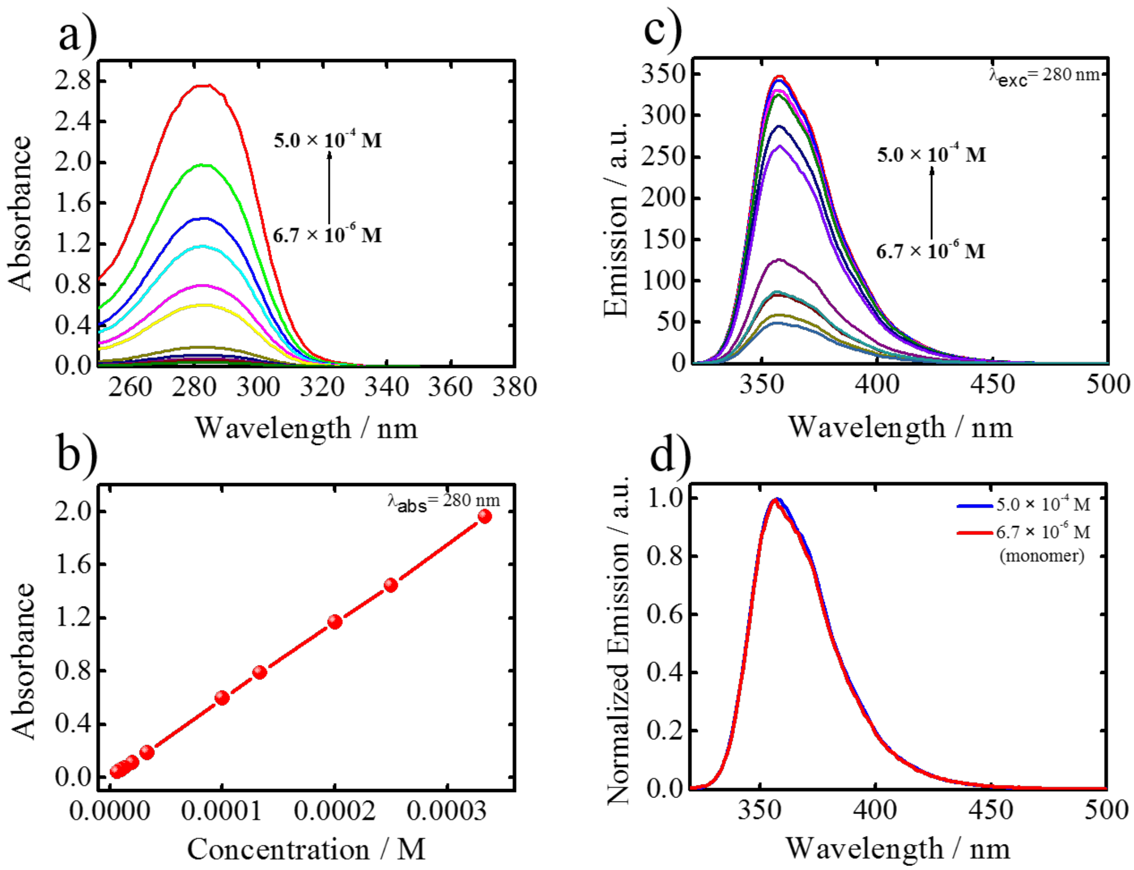


**Figure S9**. Supramolecular organization of **BTB** in the solution at different solution concentrations. Panel (a) Absorption spectra of **BTB** at different solution concentrations. Panel (b) Absorbance versus concentration at 280 nm. Panel (c) Emission spectra of **BTB** at different solution concentrations. Panel (d) Normalized emission spectra of **BTB** at high and lowest solution concentration.

In order to explore, whether **BTB** forms new species in the HA solution, UV-vis spectroscopy has been used at different solution concentrations. Figure S9a shows concentration dependent absorption spectra of **BTB**. The spectra shape of BTB remains constant and independent of the solution concentration. The absorbance increases with increasing concentration of **BTB** in the solution according to the Beer – Lambert law (Figure S9b). This indicates that only one species, probably the monomer, is absorbing, independent of concentration. The presence of only monomer has also been confirmed by emission spectra. Figure S9c shows the concentration dependent emission spectra of **BTB**, and in Figure S9d, the normalized emission intensity obtained at the highest and lowest concentration are shown. The spectral shape of the emission spectra do not depend on concentration. These results indicate that only the monomer is emitting at the entire concentration range. Therefore, from the concentration dependent absorption and emission spectra, it is clearly that **BTB** exists as monomer in solution.

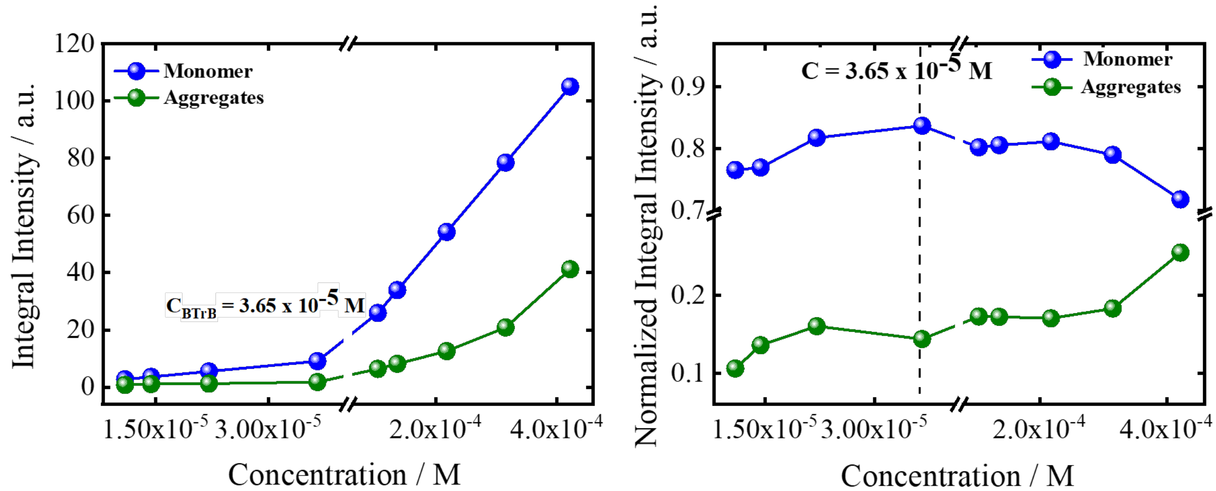


**Figure S10**. (a) Integral intensity and (b) normalized integral intensity of **BT$_r$B** monomers and aggregates as a function of concentration

The integral intensity values were obtained by calculating the area under the curve of each absorption spectra. Figure S10b plots the normalized relative contribution (normalized integral intensity) of both species to the absorption spectrum as a function of **BT$_r$B** concentration. The area of each spectrum was then normalized with the area of this total spectrum, and is further referred to as the "normalized integral intensity".

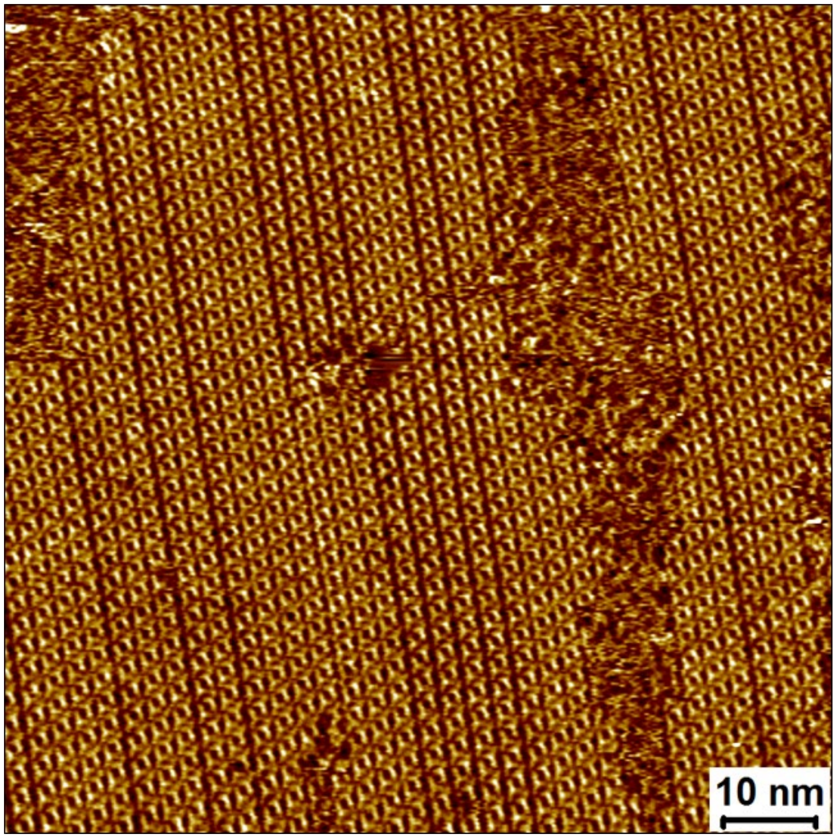


**Figure S11**. Large-scale STM image of **BT$_r$B** highest density compact network formed after annealing the sample at HA/HOPG interface ($C_{BTrB}$ = 4.2 × $10^{-4}$ M to $C_{BTrB}$ = 1.0 × $10^{-5}$ M) Imaging parameters: $I_{set}$ = 80 pA, $V_{bias}$ = -1.0 V

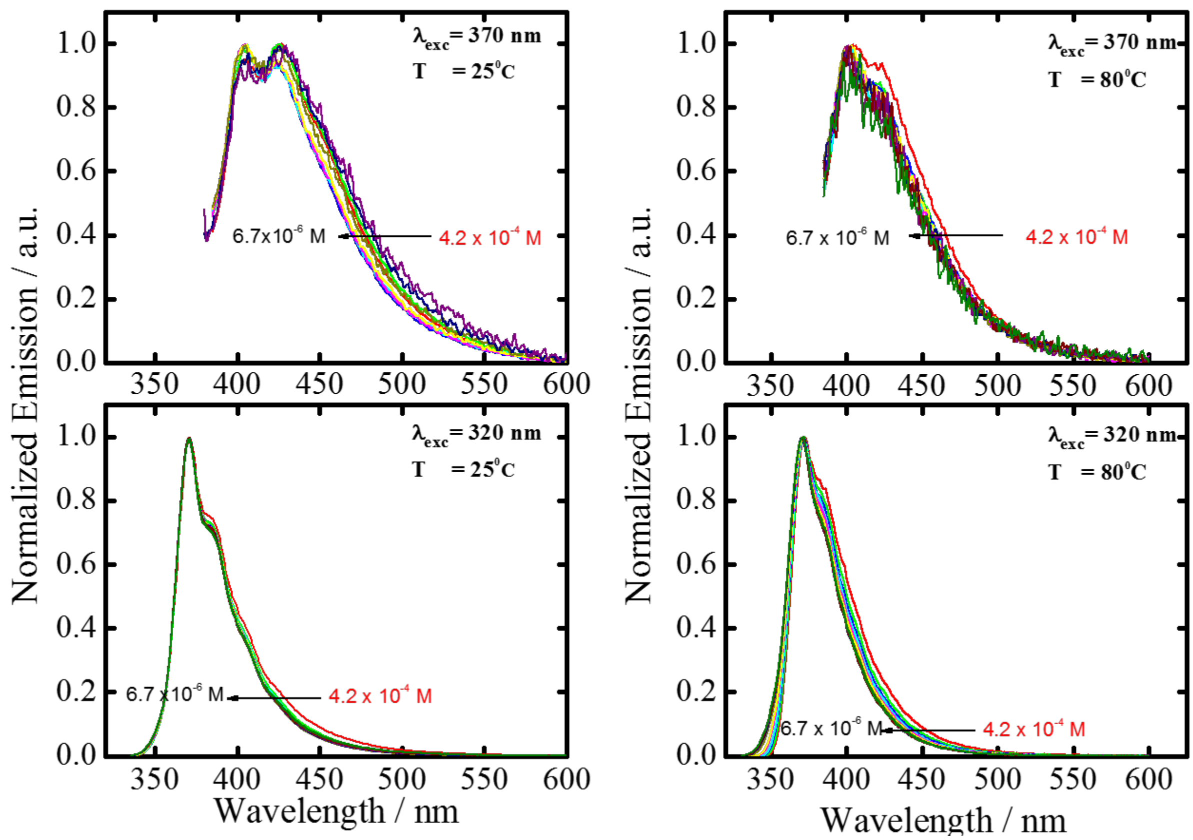


**Figure S12**. Temperature dependent emission spectra at different excitation wavelengths.