Supporting Information

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Alternating hetero H-aggregation of different dyes by interstrand stacking from two DNA-dye conjugates

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Supplemental Figure 1. Schematic representation of the electronic transitions in a monomer, H aggregate, and J aggregate on the basis of the interaction between molecular excitons in aggregates (arrows represent the transition moment of the dye), where α is the slip angle between molecules. When the dyes are stacked along the vertical axis of the dye plane (α = 90°), hypsochromic shift is induced (H aggregate). In particular, when the excitons are strongly coupled (namely, dye molecules are highly ordered), both extreme narrowing and a large hypsochromic shift of the band are induced, which is called an H*-band (H*-aggregate). The degree of bathochromic or hypsochromic shift depends on the aggregation size as well as the slip angle α: large bathochromic or hypsochromic shifts are induced when the size of the aggregate increases.
Supplemental Figure 2. UV-Vis spectra of the single-stranded MS1A (red) and NS1B (blue) that involve a single chromophore in the middle of the DNA at 0 °C, pH 5.0 in the presence of 100 mM NaCl. [DNA] = 5 µM.

The absorption maxima of MS1A and NS1B slightly shift to longer wavelength compared to those of corresponding monophosphates of respective dyes. This will probably be due to the difference of local environment around the dye.

MS1A: 5'-GGT-ATC-MS-GCA-ATC-3'
NS1B: 3'-CCA-TAG-SN-CGT-TAG-5'
Supplemental Figure 3. Melting curves of MS3A/NS3B (red) and natural NA/NB (blue) without artificial residues at pH 5.0 (10 mM MES buffer) in the presence of 100 mM NaCl. The melting temperature ($T_m$) of MS3A/NS3B was determined as 50.7 °C, which was much higher than that of natural NA/NB (39.8 °C). The stabilization of MS3A/NS3B duplex is probably due to the stacking interaction between dyes and electrostatic interactions between negative phosphate groups and positive Naphthyl Red moieties.

Sequences:

**MS3A:** 5'-GGT-ATC-MSMSMS-GCA-ATC-3'
**NS3B:** 3'-CCA-TAG-SNSNSN-CGT-TAG-5'
**NA:** 5'-GGT-ATC-GCA-ATC-3'
**NB:** 3'-CCA-TAG-CGT-TAG-5'

M and N represent Methyl Red and Naphthyl Red moieties, respectively. See Supplemental Figure 5 or Scheme 1b in the main text for the structures.
Supplemental Figure 4. UV-Vis spectra of MS3A/NS3B (red), MS2A/NS2B (blue) and MS1A/NS1B (green) at 0 °C, pH 5.0 (10 mM MES buffer) in the presence of 100 mM NaCl. Concentration of each strand was 5.0 µM.

Sequences:

**MS3A**: 5'-GGT-ATC-\textit{MSMSMS}-GCA-ATC-3'  
**NS3B**: 3'-CCA-TAG-\textit{SNNSNSN}-CGT-TAG-5'  
**MS2A**: 5'-GGT-ATC-\textit{MSMS}-GCA-ATC-3'  
**NS2B**: 3'-CCA-TAG-\textit{SNNSN}-CGT-TAG-5'  
**MS1A**: 5'-GGT-ATC-\textit{MS}-GCA-ATC-3'  
**NS1B**: 3'-CCA-TAG-\textit{SN}-CGT-TAG-5'  

M and N represent Methyl Red and Naphthyl Red moieties, respectively. See Supplemental Figure 3 or Scheme 1b in the main text for the structures.

Axial stacking of identical dye molecules, H-aggregation, is known to cause hypsochromic shift, and the degree of hypsochromic shift depends on the number of molecules aggregating. In the case of conventional homo H-aggregation, an increase in the aggregation number causes a larger hypsochromic shift due to the exciton coupling among the chromophores as predicted from the molecular exciton theory. But as demonstrated in this figure, a similar larger hypsochromic shift was also induced by the increase in the aggregation number for the hetero aggregation, indicating that the new band induced by the hetero aggregation is the H-band.
Supplemental Figure 5. UV-Vis spectra of Azobenzene (AS3B; red), Methyl Red (MS3A; blue) and Naphthyl Red (NS3A; green) at pH 5.0 (10 mM MES buffer), at 0 °C, in the presence of 100 mM NaCl.

Sequences:

**AS3B**: 5’-GGT-ATC-ASASAS-GCA-ATC-3’

**MS3A**: 5’-GAT-TGC-MSMSMS-GAT-ACC-3’

**NS3A**: 5’-GAT-TGC-NSNSNS-GAT-ACC-3’

A, M and N represent azobenzene, Methyl Red and Naphthyl Red moieties as shown below, respectively.