Supplementary information

Towards tunable exciton delocalization in DNA Holliday junction-templated indodicarbocyanine 5 (Cy5) dye derivatives heterodimers

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Contents

SI-1. DNA construct synthesis

Table S1. Nucleotide sequences to synthesize DNA HJ.

DNA	DNA sequence (5'-3')	Cy5-DNA sequence (5'-3')
Strand A	ATATAATCGCTCGCATATTATGACTG	ATATAATCGCTCG-**X**-CATATTATGACTG
Strand B	CAGTCATAATATGTGGAATGTGAGTG	CAGTCATAATATG-**X**-TGGAATGTGAGTG
Strand C	CACTCACATTCCACTCAACACCACAA	CACTCACATTCCA-**X**-CTCAACACCACAA
Strand D	TTGTGGTGTTGAGCGAGCGATTATAT	TTGTGGTGTTGAG-**X**-CGAGCGATTATAT

The designed DNA-HJ is an immobile and stable structure because the DNA sequence and the base pairs are non-complementary in the center vicinity of the branch point preventing branch migration (see Section SI-5).

Desired labeled DNA strands with Cy5-R (blue X) and their complementary non-labeled strands (DNA without dye) were used to synthesize the DNA-HJ constructs. All DNA constructs were annealed in an Eppendorf Mastercycler (Eppendorf; Hamburg, Germany) using the following thermal cycling protocol: 95 °C for 5 minutes, cooled to 85 °C at a rate of 5 minutes/1 °C drop, held at 85 °C for 10 minutes, then cooled to 4 °C at a cooling rate of 10 minutes/1 °C drop with the lid temperature fixed at 95 °C. Samples were stored at 4 °C until use for experiments.

SI-2. Optical characterization of monomers

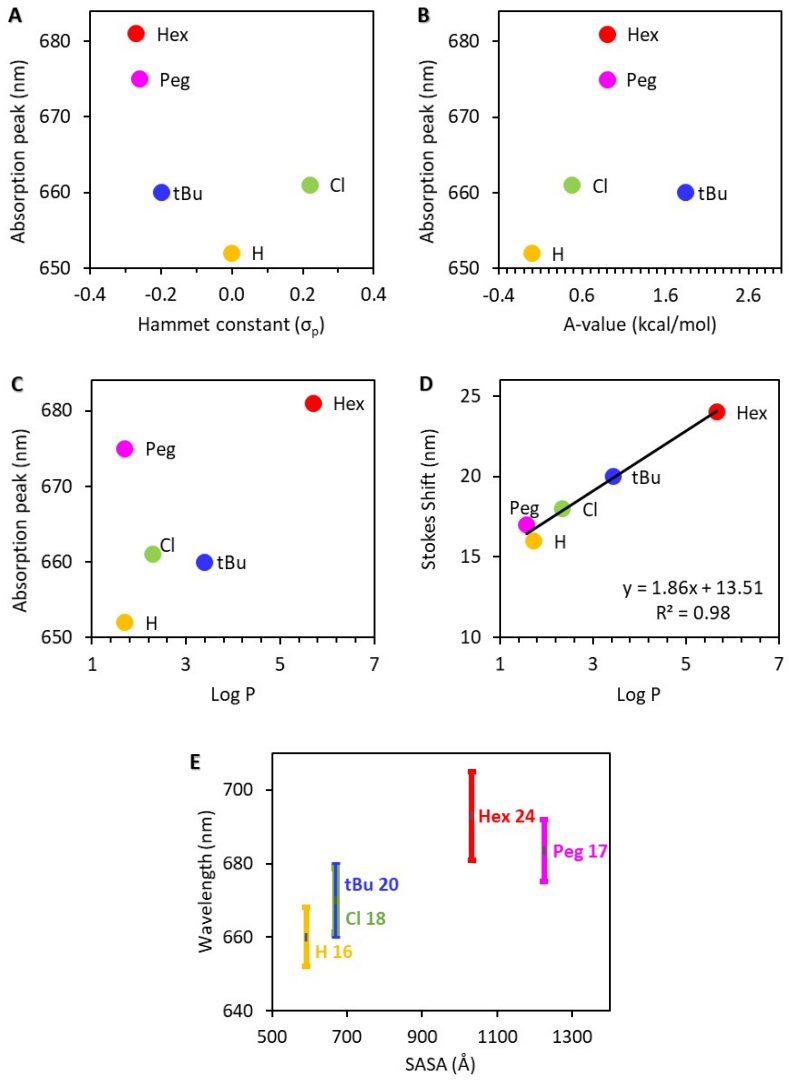

Figure S1. Relationship between the maximum absorption peak of monomers and [A] the electron-withdrawing capacity of R substituents measured by the Hammet constant in *para* position (σ_p), [B] Bulkiness of the substituents measured by the A-value (kcal/mol), and [C] hydrophobicity of the modified Cy5-R measured by Log P. [D] depicts the relationship between Stokes shift and Log P and [E] depicts the relationship between the solvent accessible area (SASA, Å^2) and the positions of absorption and emission peaks depicted by bars. The difference in emission and absorption peak ($\Delta\lambda$ in nm) is known as the Stokes shift, which represents the spectral shift to lower energy between the incident light (absorption peak) and emitted light (emission peak

SI-3. Optical characterization of adjacent AB and transverse AC Cy5-R heterodimers

SI-3.1. Normalized absorption and fluorescence spectra

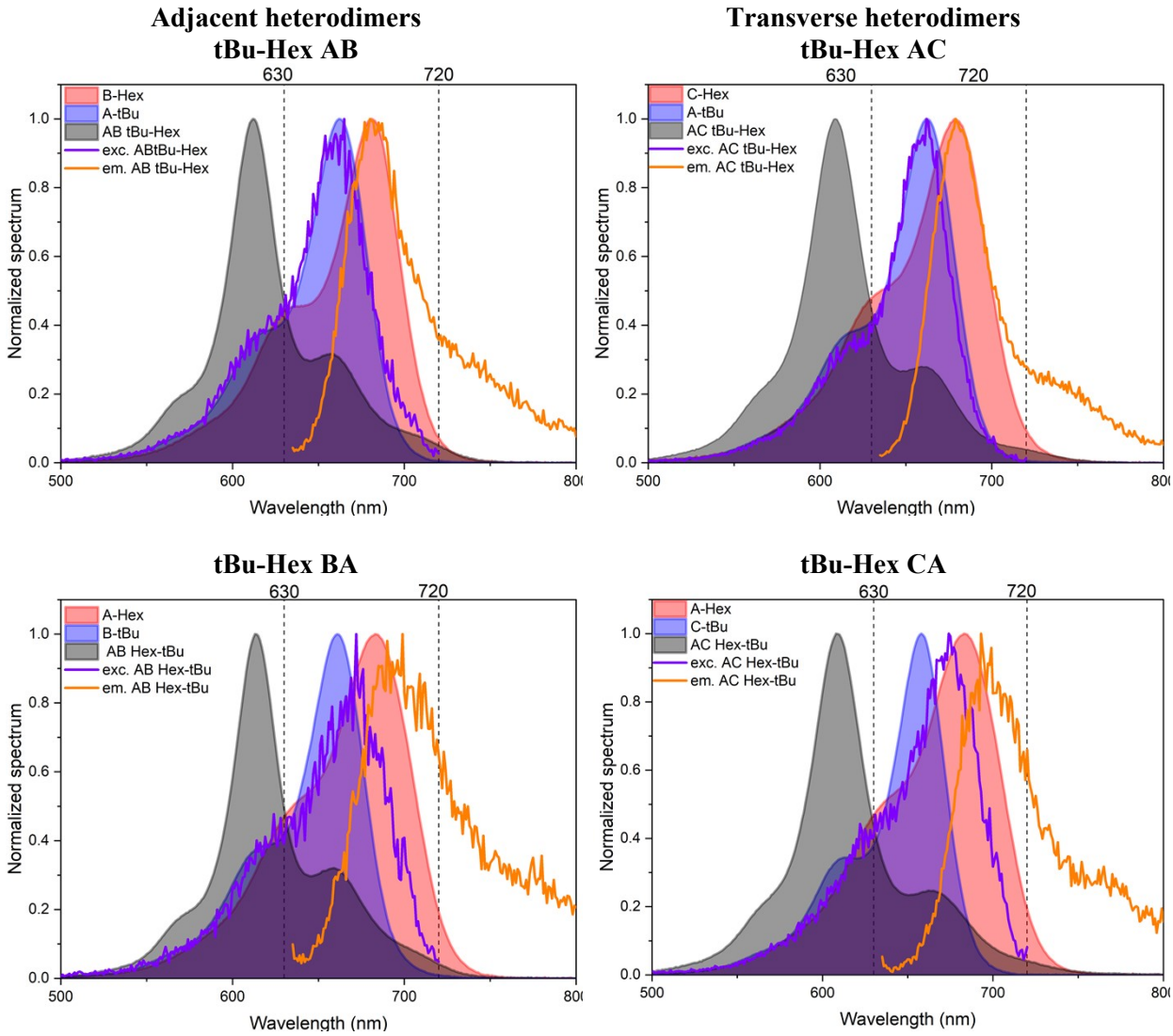

Figure S2. Normalized absorption spectra of monomers and heterodimers tBu-Hex (shadow) and excitation (emitted at 720 nm) and emission (excited at 630 nm) spectra of heterodimers (solid lines). All dye-DNA constructs are templated by DNA HJ.

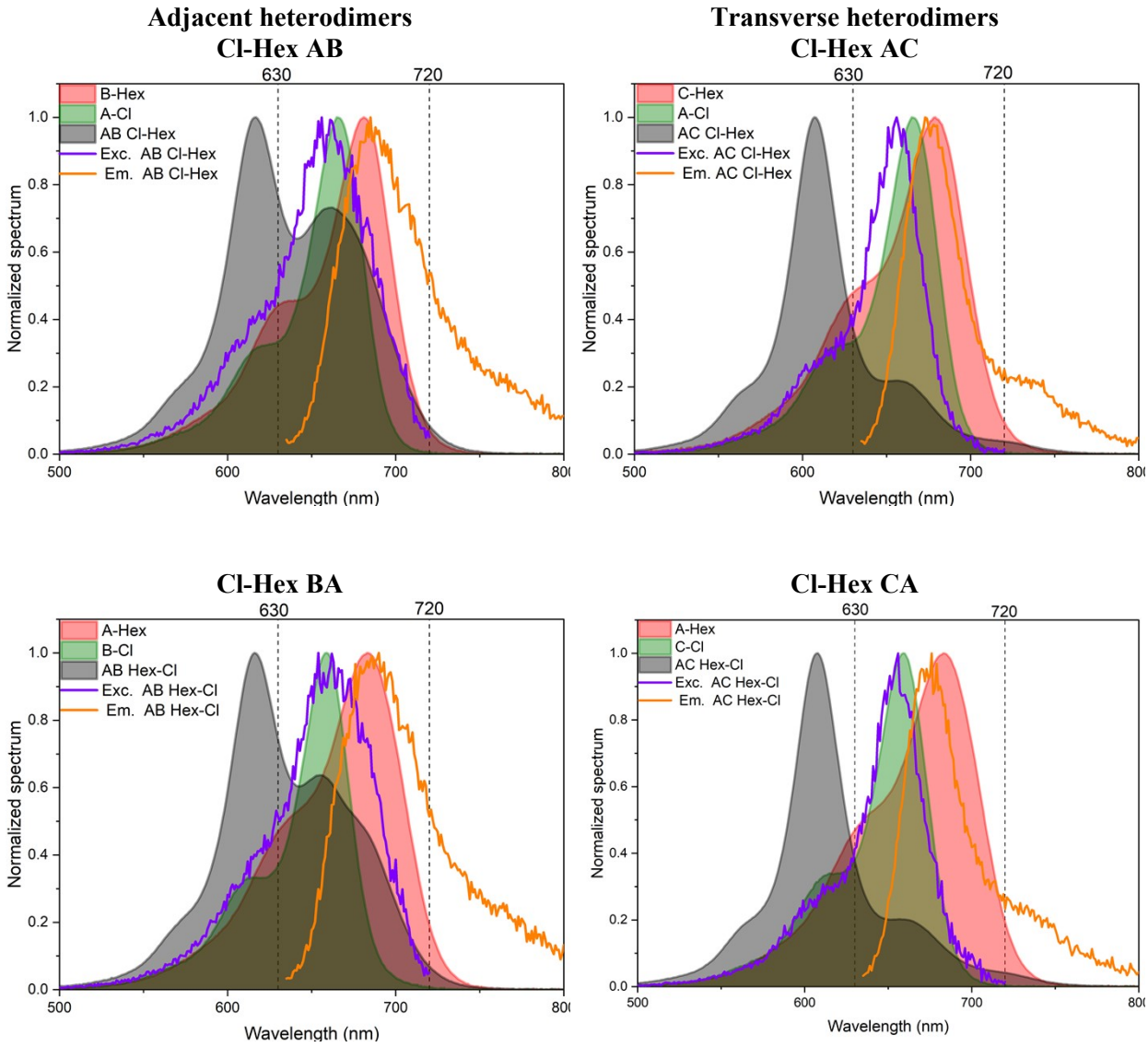

Figure S3. Normalized absorption spectra of monomers and heterodimers Cl-Hex (shadow) and excitation (emitted at 720 nm) and emission (excited at 630 nm) spectra of heterodimers (solid lines). All dye-DNA constructs are templated by DNA HJ.

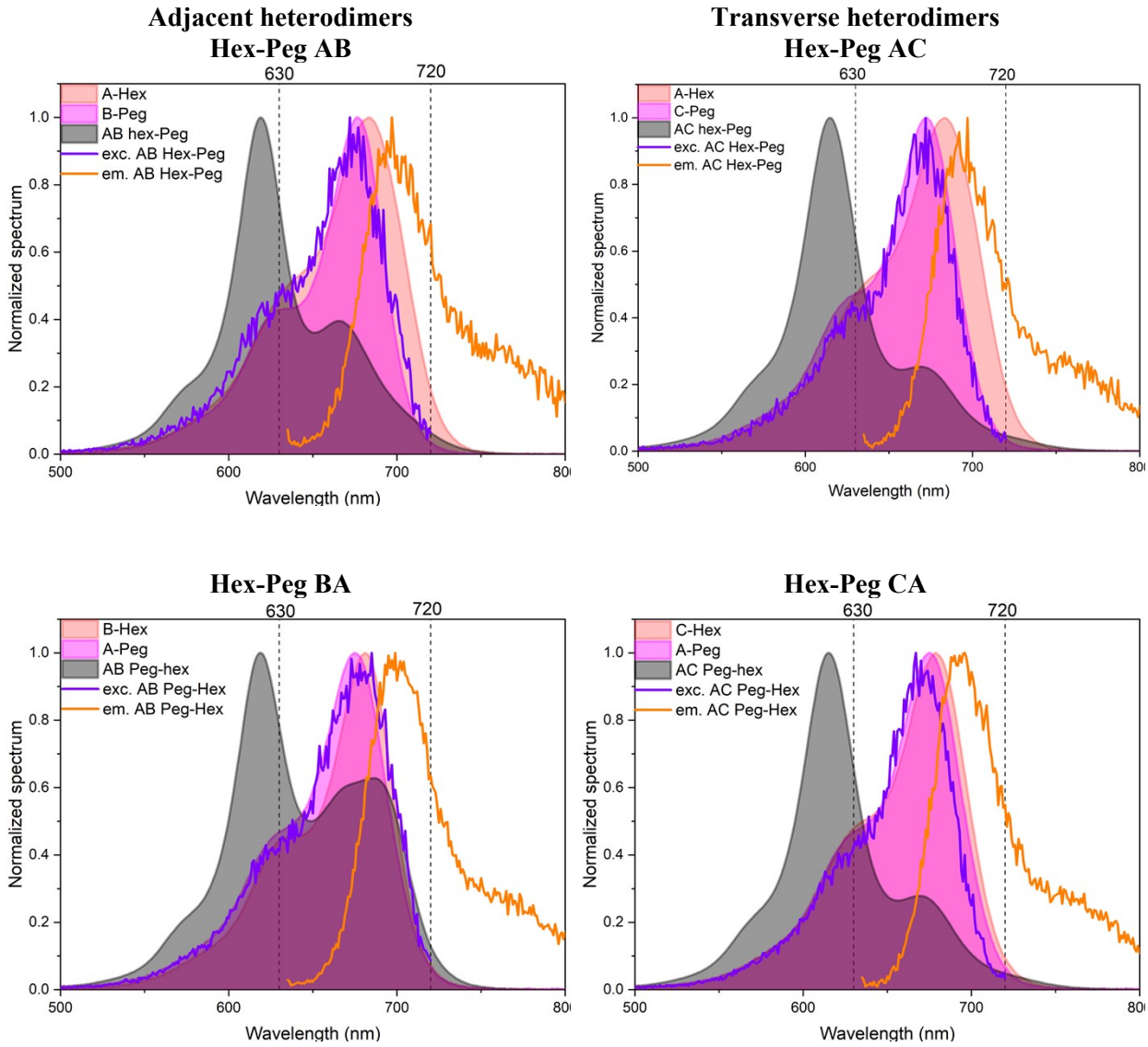

Figure S4. Normalized absorption spectra of monomers and heterodimers Hex-Peg (shadow) and excitation (emitted at 720 nm) and emission (excited at 630 nm) spectra of heterodimers (solid lines). All dye-DNA constructs are templated by DNA HJ.

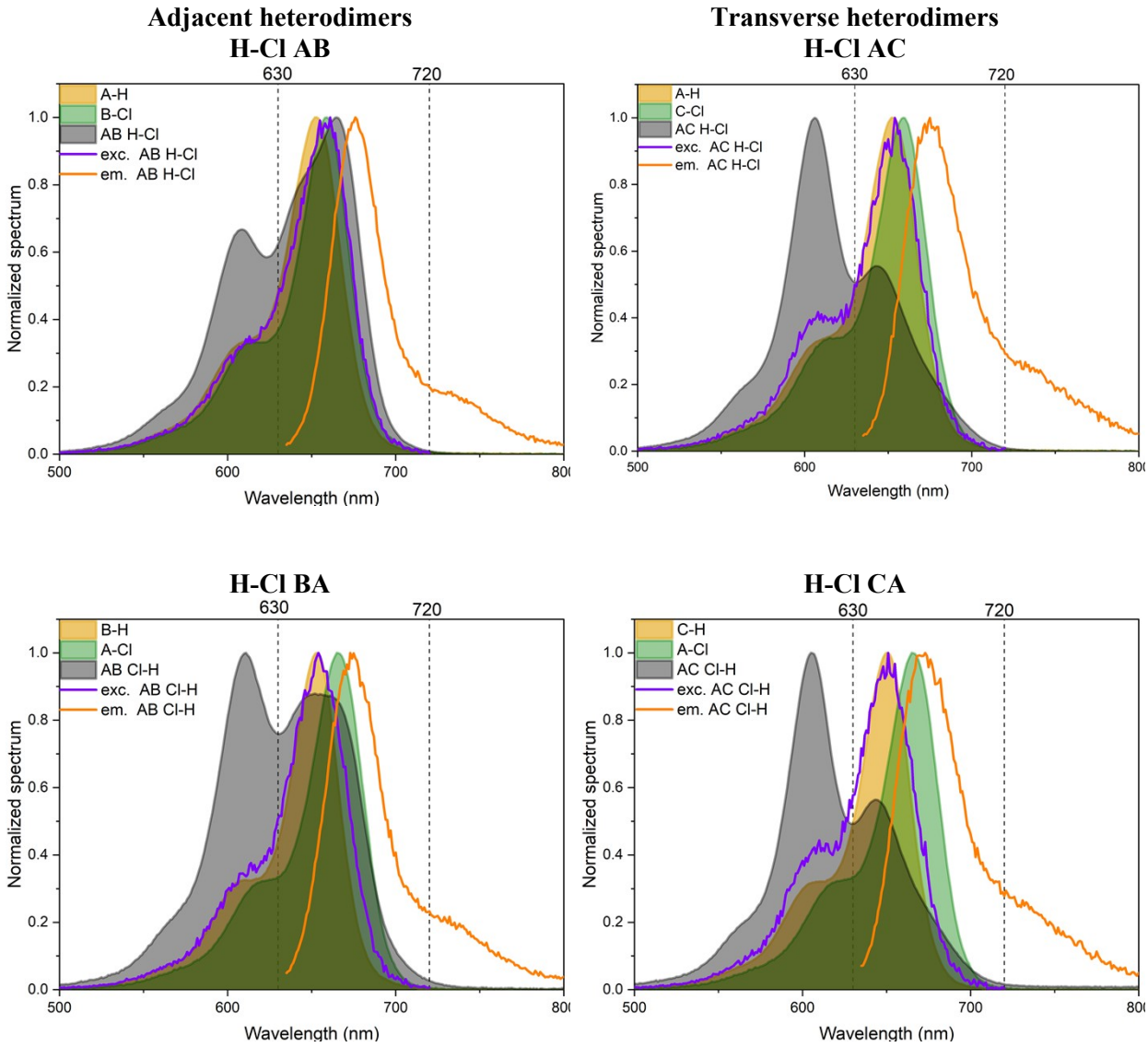

Figure S5. Normalized absorption spectra of monomers and heterodimers Cl-Hex (shadow) and excitation (emitted at 720 nm) and emission (excited at 630 nm) spectra of heterodimers (solid lines). All dye-DNA constructs are templated by DNA HJ.

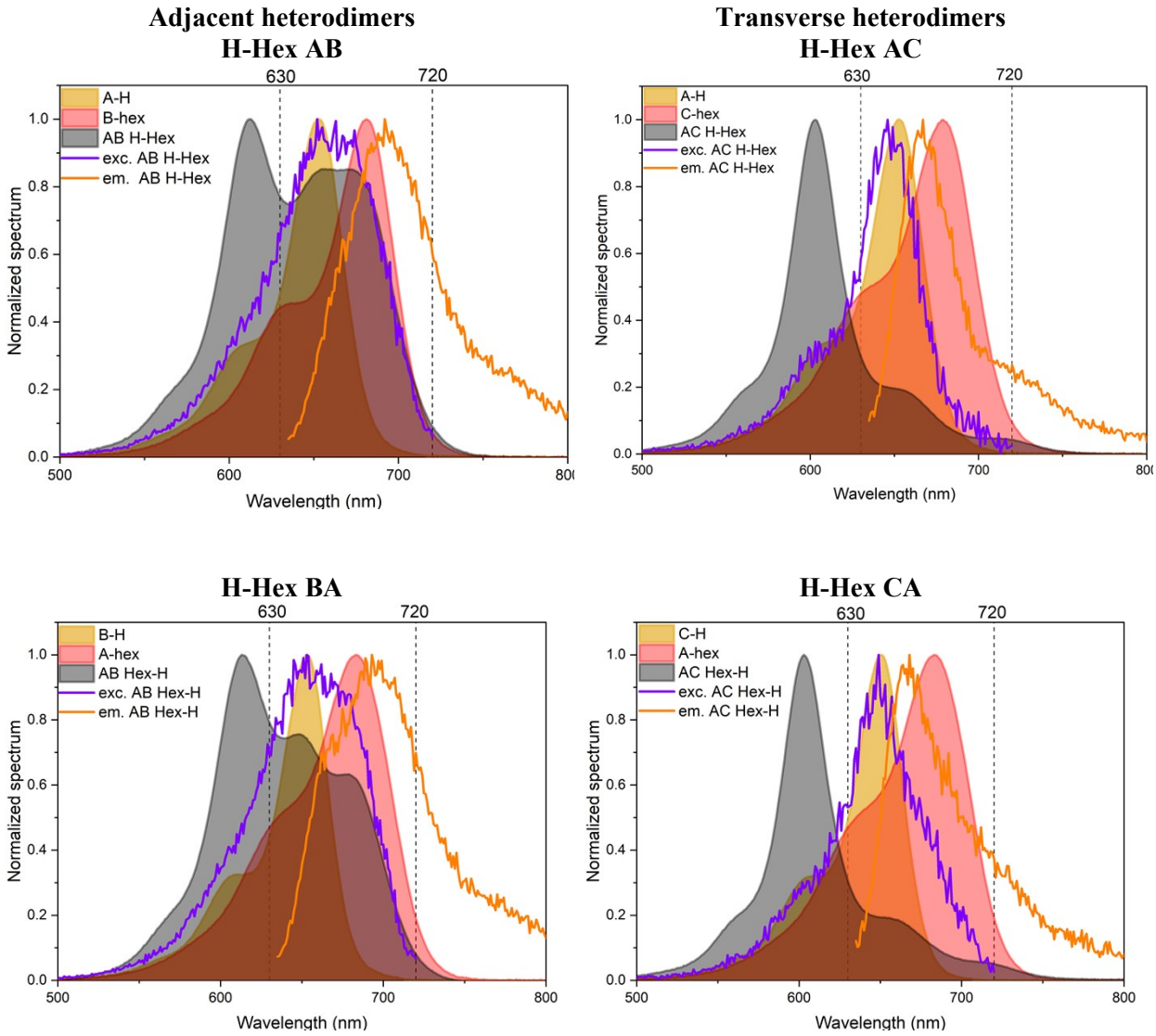

Figure S6. Normalized absorption spectra of monomers and heterodimers H-Hex (shadow) and excitation (emitted at 720 nm) and emission (excited at 630 nm) spectra of heterodimers (solid lines). All dye-DNA constructs are templated by DNA HJ.

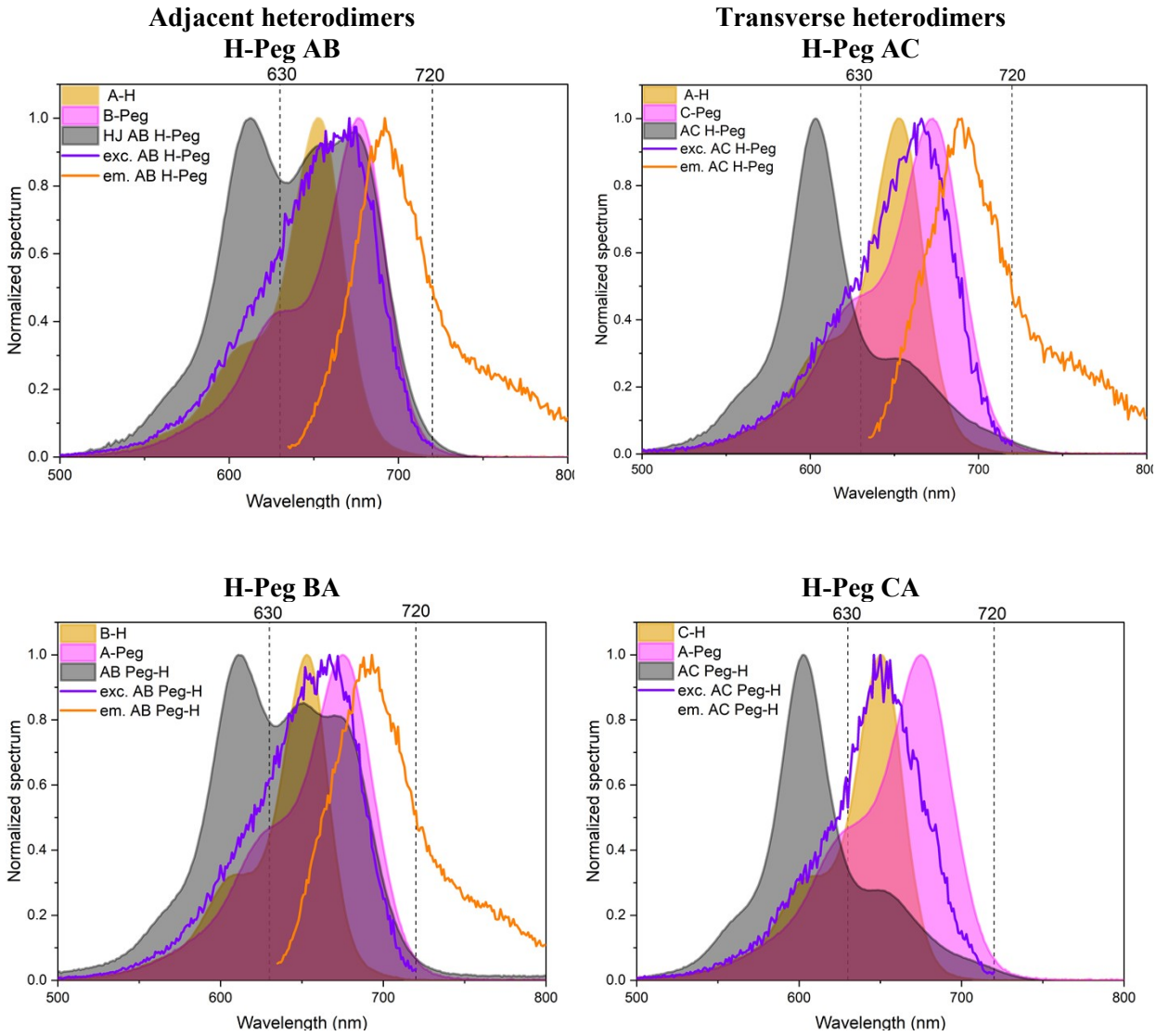

Figure S7. Normalized absorption spectra of monomers and heterodimers H-Peg (shadow) and excitation (emitted at 720 nm) and emission (excited at 630 nm) spectra of heterodimers (solid lines). All dye-DNA constructs are templated by DNA HJ.

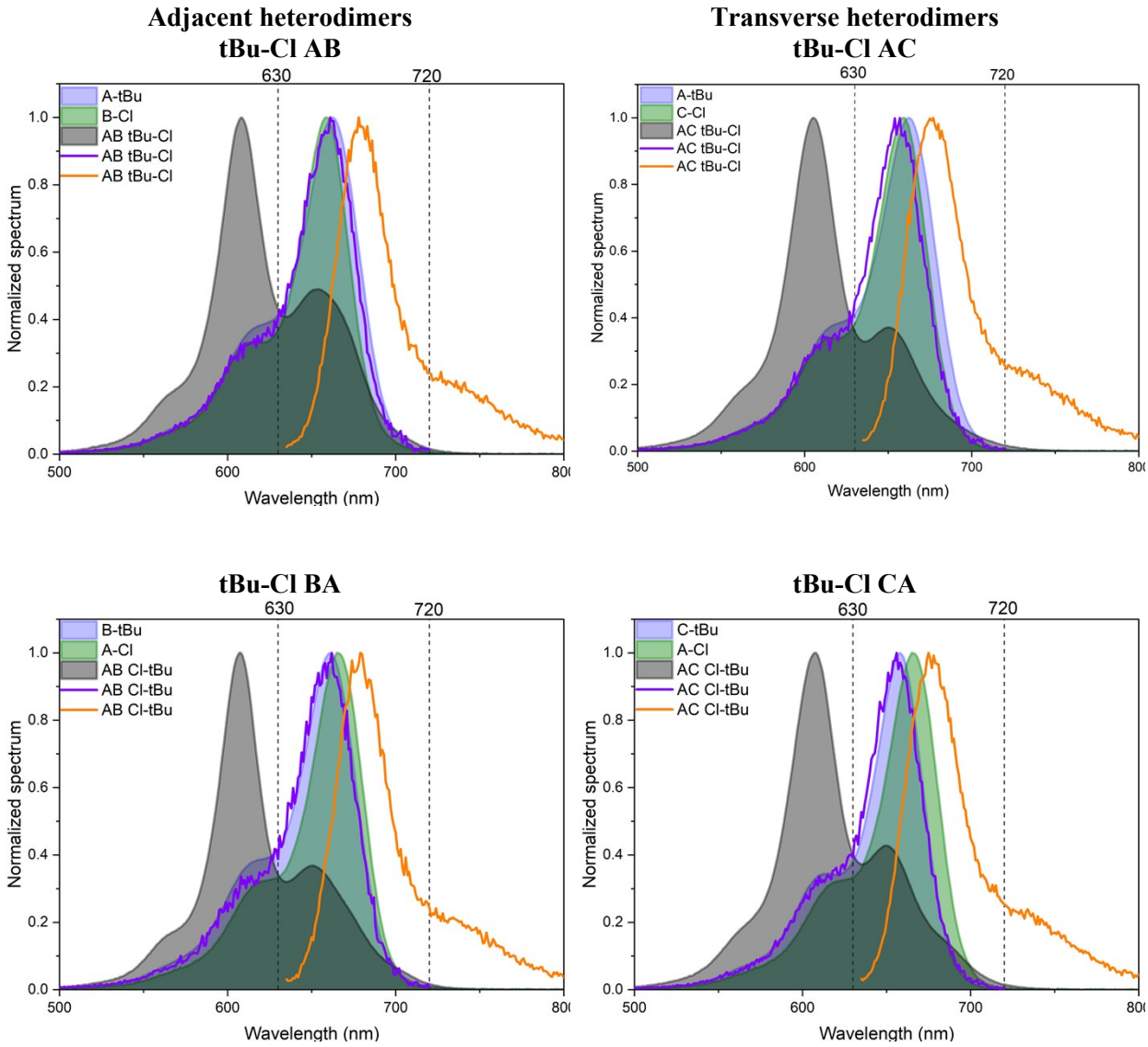

Figure S8. Normalized absorption spectra of monomers and heterodimers tBu-Cl (shadow) and excitation (emitted at 720 nm) and emission (excited at 630 nm) spectra of heterodimers (solid lines). All dye-DNA constructs are templated by DNA HJ.

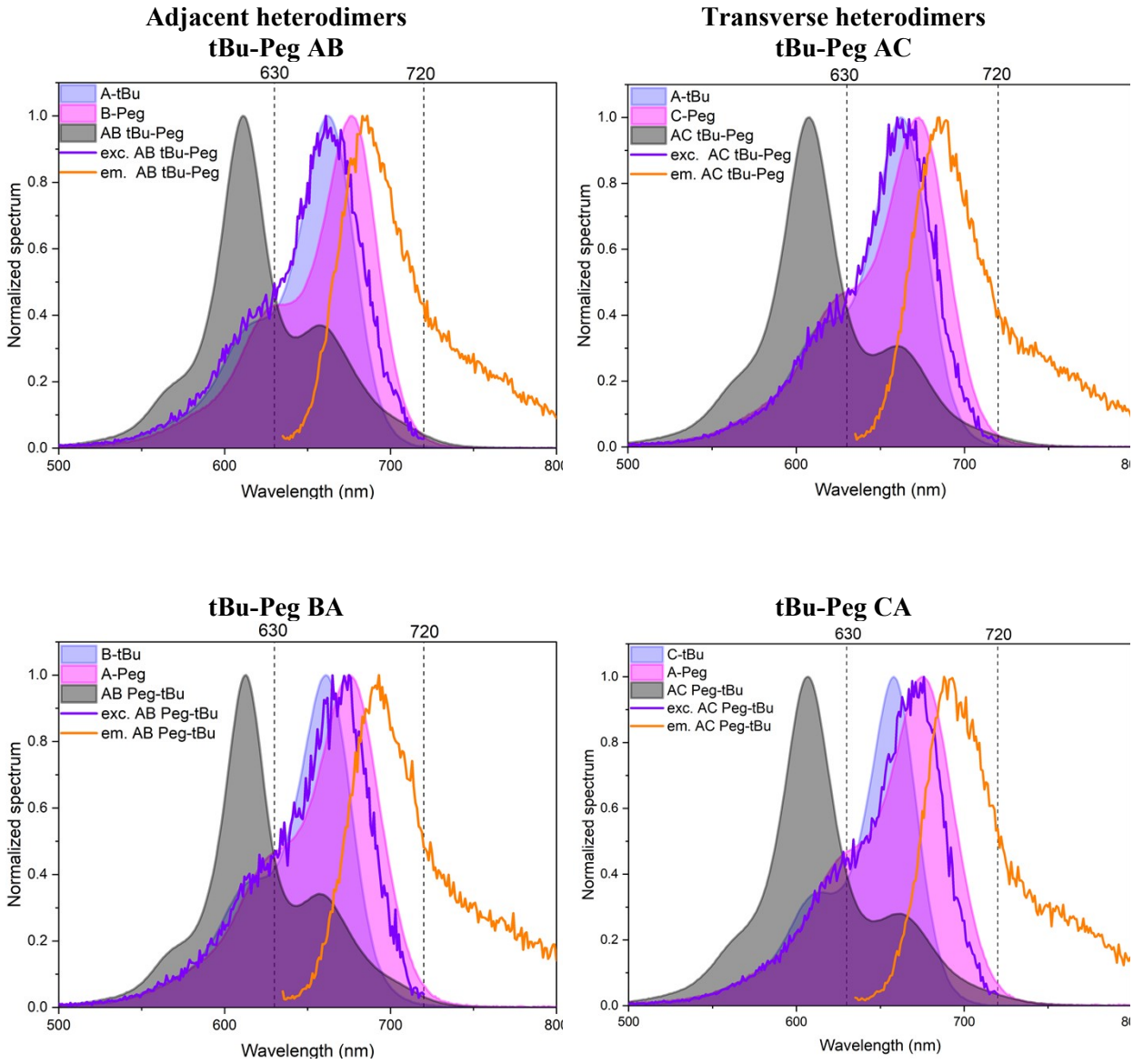

Figure S9. Normalized absorption spectra of monomers and heterodimers tBu-Peg (shadow) and excitation (emitted at 720 nm) and emission (excited at 630 nm) spectra of heterodimers (solid lines). All dye-DNA constructs are templated by DNA HJ.

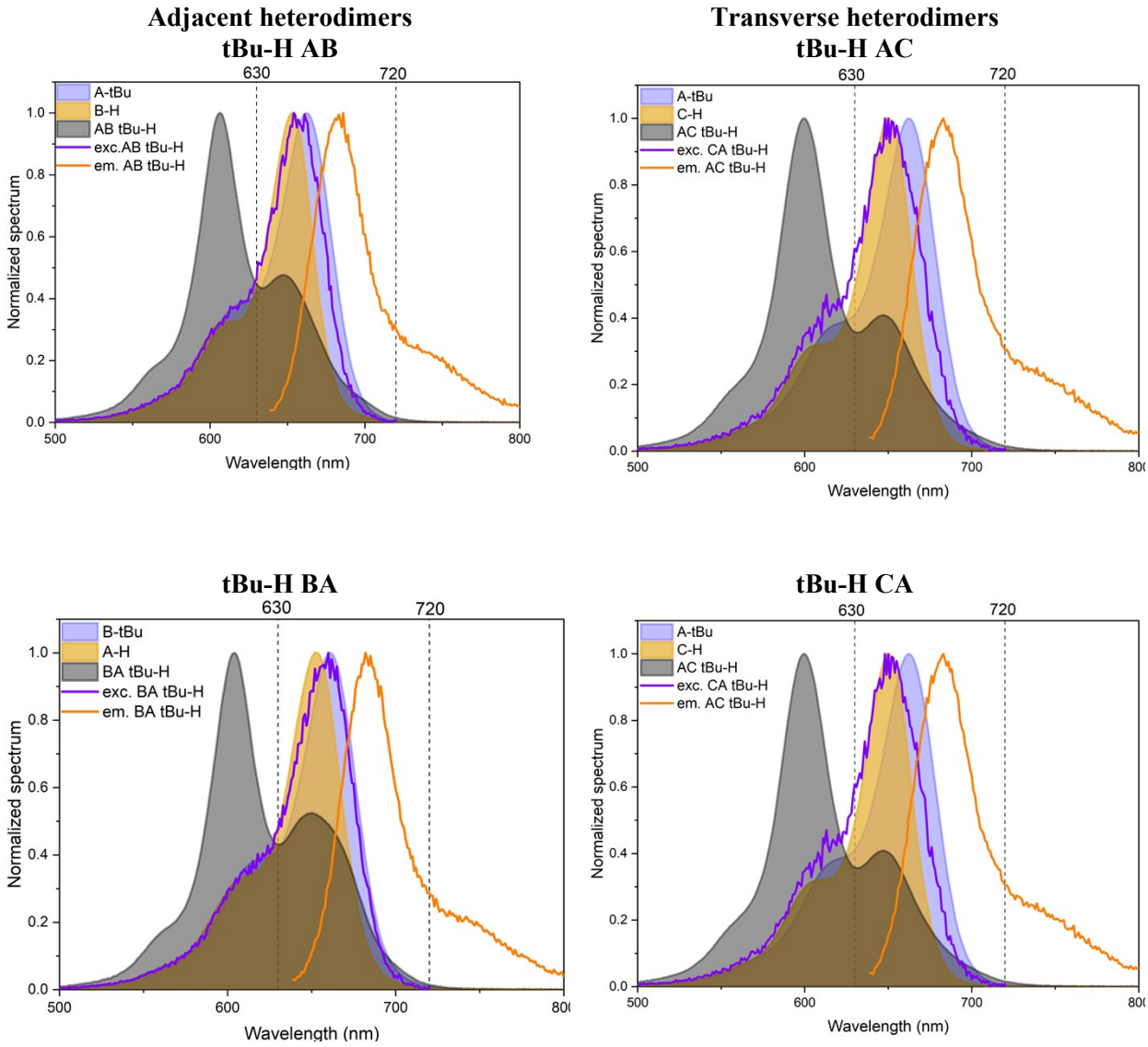

Figure S10. Normalized absorption spectra of monomers and heterodimers tBu-H (in shadow) and excitation (emitted at 720 nm) and emission (excited at 630 nm) spectra of heterodimers (solid lines). All dye-DNA constructs are templated by DNA HJ

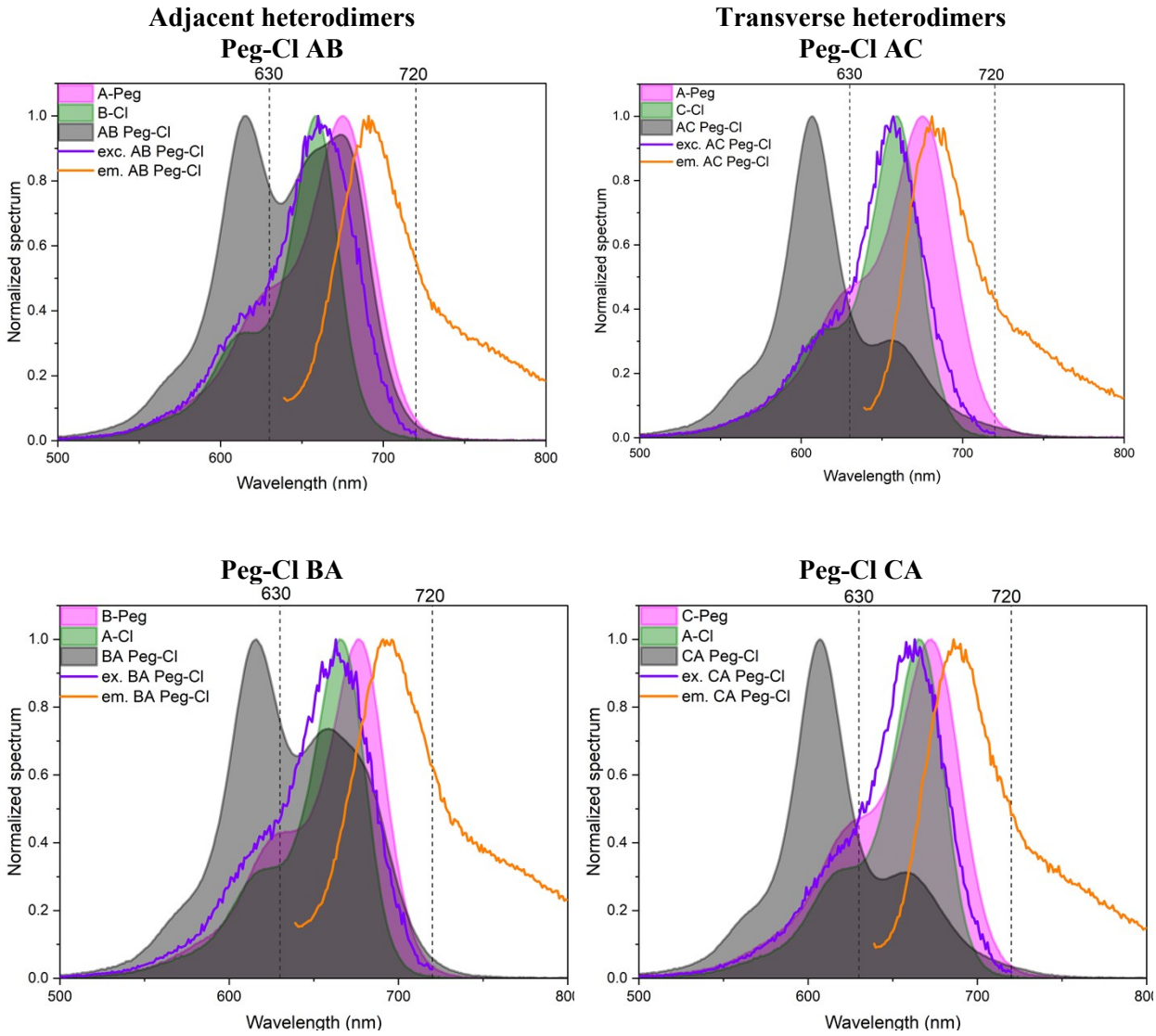

Figure S11. Normalized absorption spectra of monomers and heterodimers Peg-Cl (in shadow) and excitation (emitted at 720 nm) and emission (excited at 630 nm) spectra of heterodimers (solid lines). All dye-DNA constructs are templated by DNA HJ

SI-3.2. Absorption spectra and circular dichroism of heterodimers

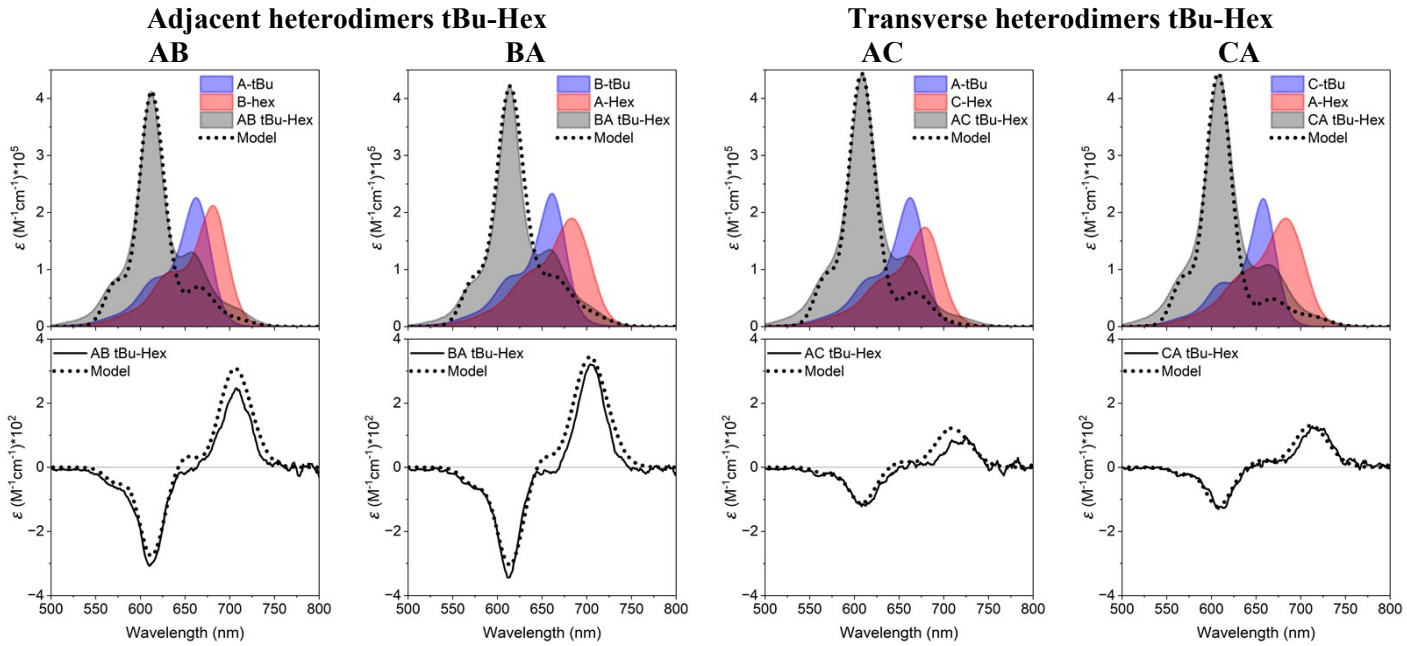

Figure S12. Optical characterization of adjacent and transverse Cy5 **tBu-Hex** heterodimers templated by DNA Holliday junction (DNA HJ). The experimental absorption (upper figures) and circular dichroism (down figures) spectra (solid line) were converted into molar extinction coefficient units (ε $M^{-1}cm^{-1}$). Dot lines depict the modeled results using the Kühn−Renger−May approach (KRM model).

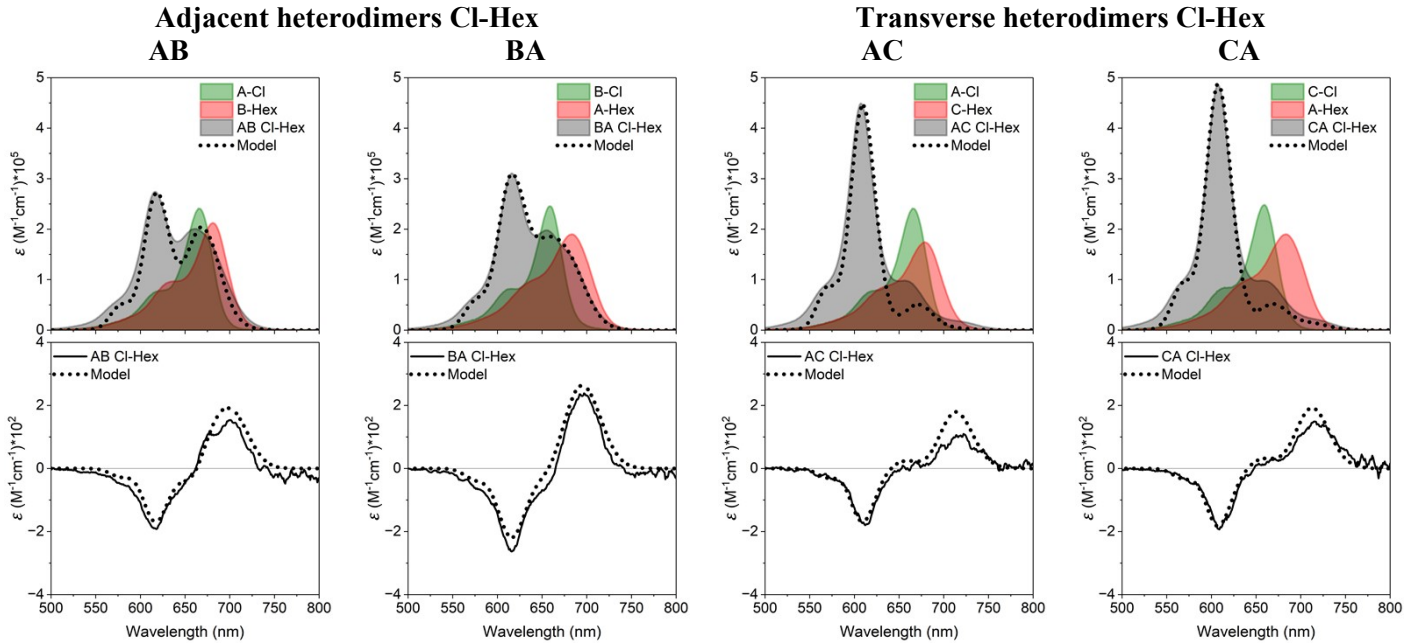

Figure S13. Optical characterization of adjacent and transverse Cy5 Cl-Hex heterodimers templated by DNA Holliday junction (DNA HJ). The experimental absorption (upper figures) and circular dichroism (down figures) spectra (solid line) were converted into molar extinction coefficient units (ε $M^{-1}cm^{-1}$). Dot lines depict the modeled results using the Kühn−Renger−May approach (KRM model).

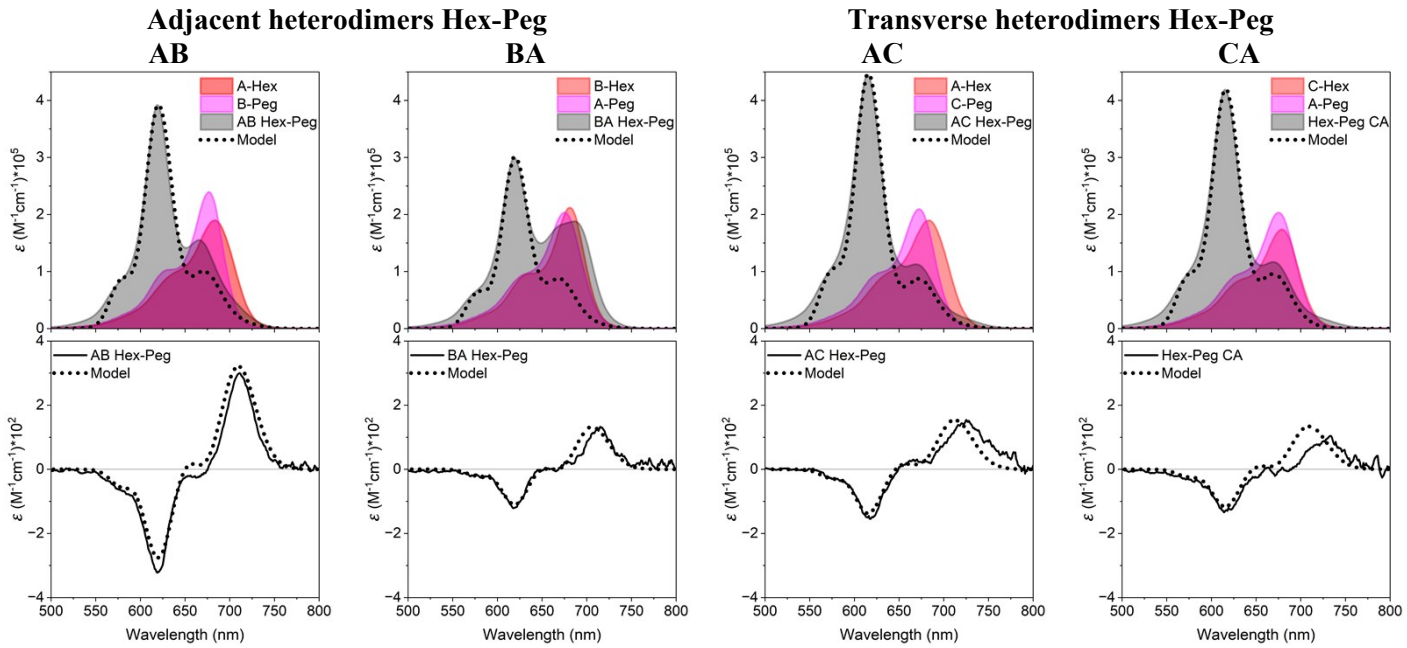

Figure S14. Optical characterization of adjacent and transverse Cy5 Hex-Peg heterodimers templated by DNA Holliday junction (DNA HJ). The experimental absorption (upper figures) and circular dichroism (down figures) spectra (solid line) were converted into molar extinction coefficient units (ε $M^{-1}cm^{-1}$). Dot lines depict the modeled results using the Kühn−Renger−May approach (KRM model).

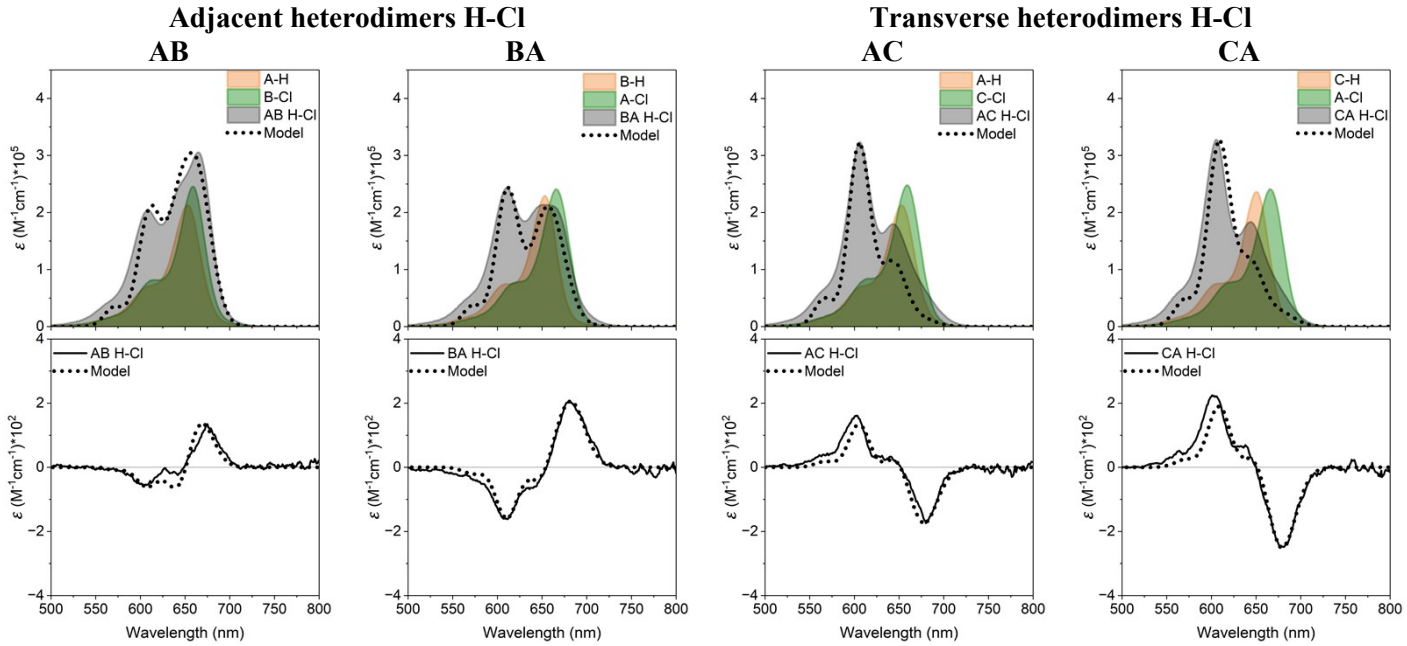

Figure S15. Optical characterization of adjacent and transverse Cy5 H-Cl heterodimers templated by DNA Holliday junction (DNA HJ). The experimental absorption (upper figures) and circular dichroism (down figures) spectra (solid line) were converted into molar extinction coefficient units (ε $M^{-1}cm^{-1}$). Dot lines depict the modeled results using the Kühn−Renger−May approach (KRM model).

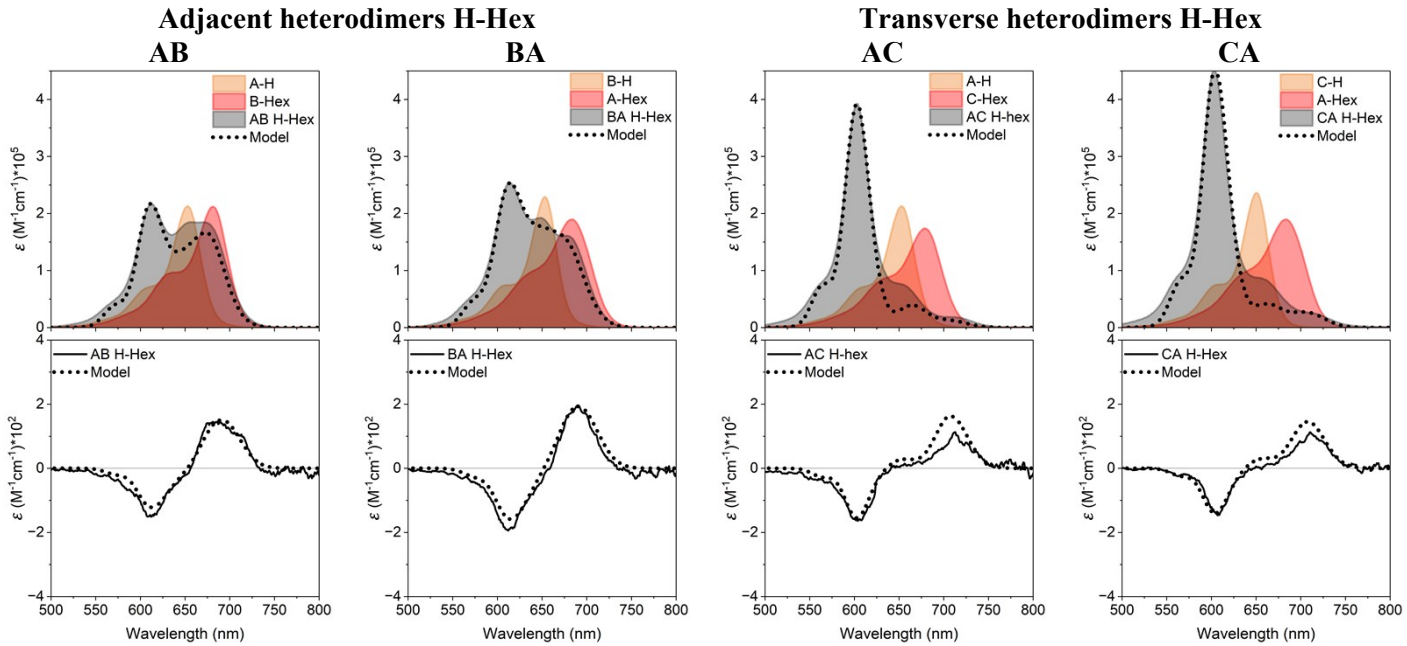

Figure S16. Optical characterization of adjacent and transverse Cy5 H-Hex heterodimers templated by DNA Holliday junction (DNA HJ). The experimental absorption (upper figures) and circular dichroism (down figures) spectra (solid line) were converted into molar extinction coefficient units ($\boldsymbol{\varepsilon}$ $M^{-1}cm^{-1}$). Dot lines depict the modeled results using the Kühn−Renger−May approach (KRM model).

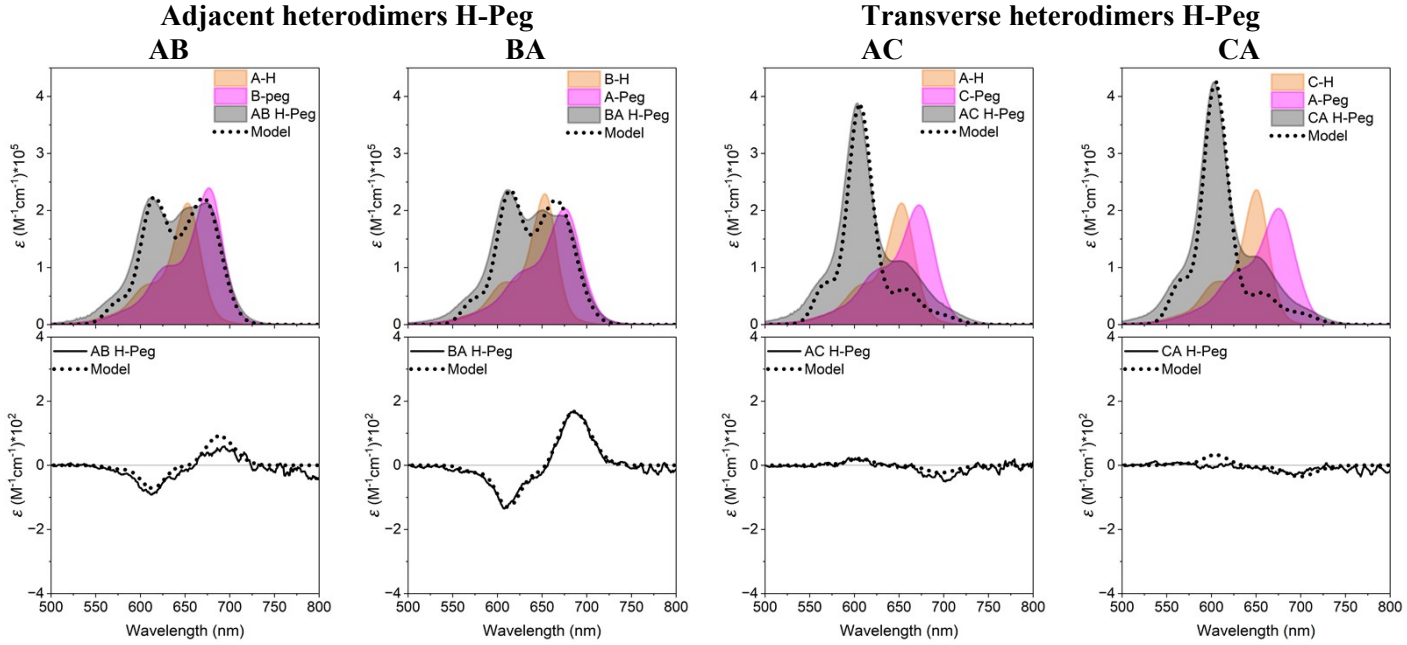

Figure S17. Optical characterization of adjacent and transverse Cy5 **H-Peg** heterodimers templated by DNA Holliday junction (DNA HJ). The experimental absorption (upper figures) and circular dichroism (down figures) spectra (solid line) were converted into molar extinction coefficient units ($\boldsymbol{\varepsilon}$ $M^{-1}cm^{-1}$). Dot lines depict the modeled results using the Kühn−Renger−May approach (KRM model).

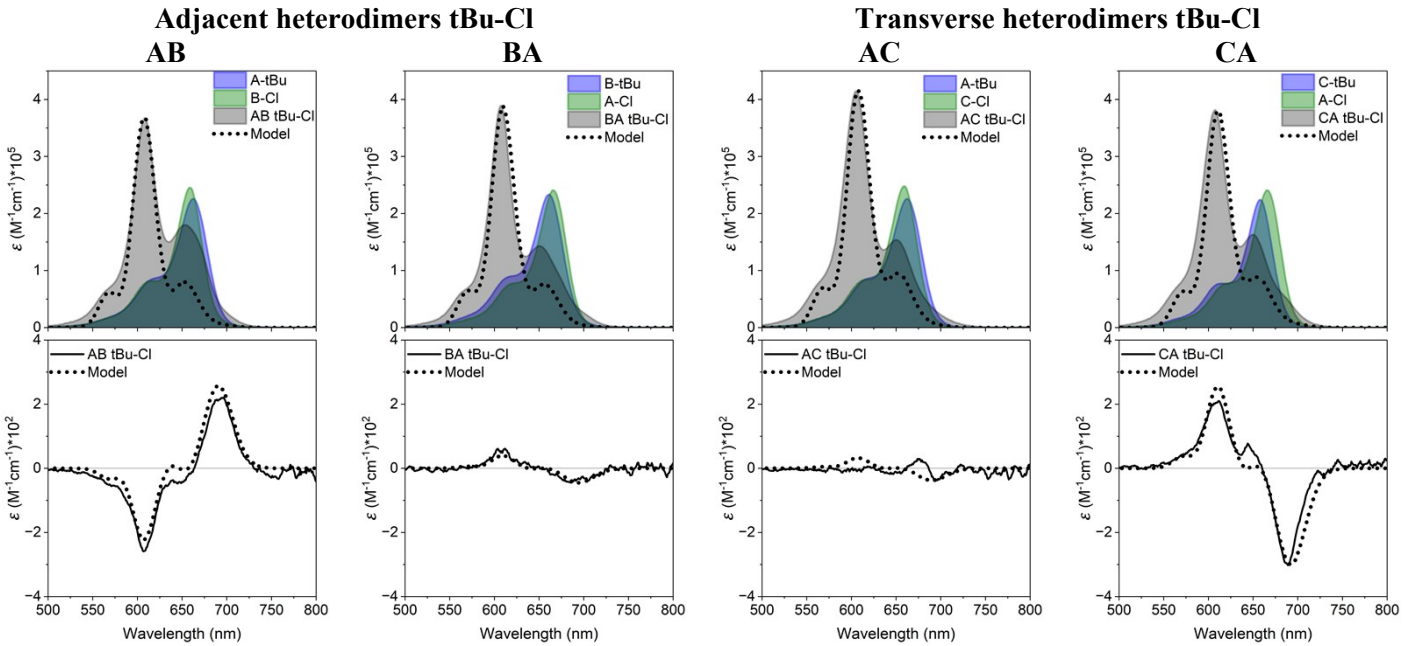

Figure S18. Optical characterization of adjacent and transverse Cy5 tBu-Cl heterodimers templated by DNA Holliday junction (DNA HJ). The experimental absorption (upper figures) and circular dichroism (down figures) spectra (solid line) were converted into molar extinction coefficient units (ε $M^{-1}cm^{-1}$). Dot lines depict the modeled results using the Kühn−Renger−May approach (KRM model).

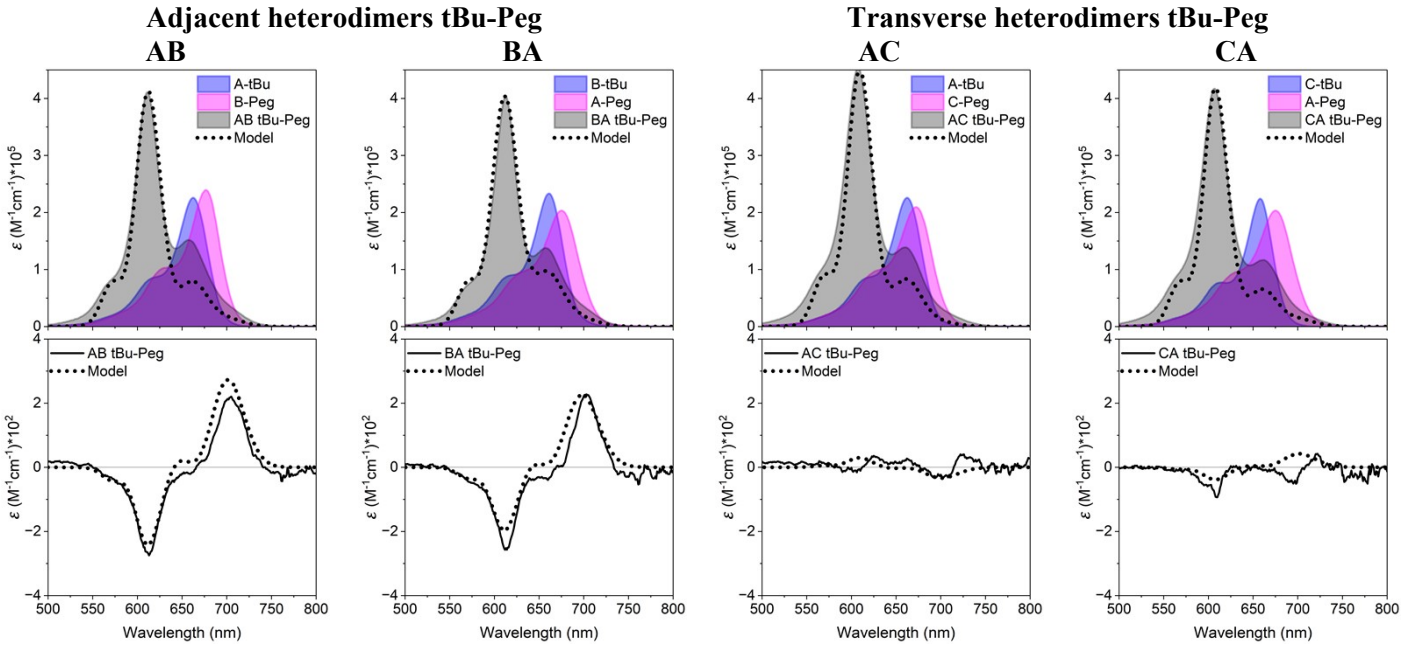

Figure S19. Optical characterization of adjacent and transverse Cy5 **tBu-Peg** heterodimers templated by DNA Holliday junction (DNA HJ). The experimental absorption (upper figures) and circular dichroism (down figures) spectra (solid line) were converted into molar extinction coefficient units (ε $M^{-1}cm^{-1}$). Dot lines depict the modeled results using the Kühn−Renger−May approach (KRM model).

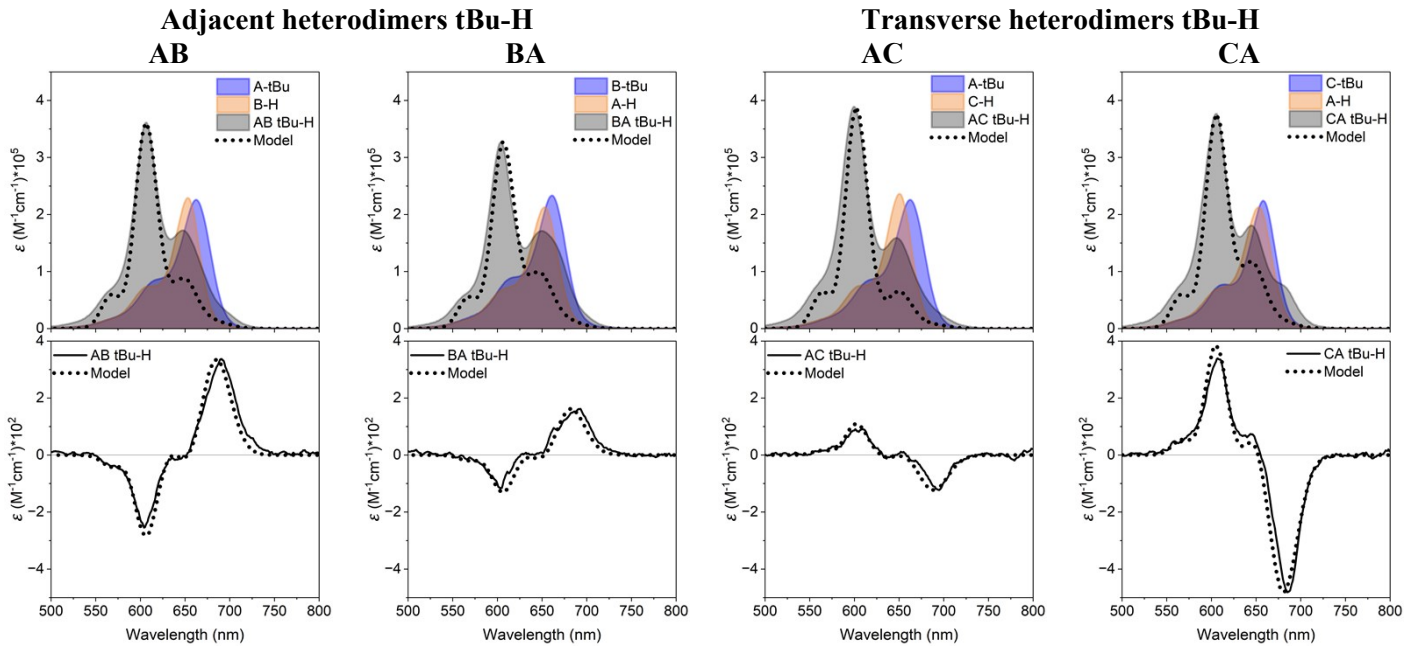

Figure S20. Optical characterization of adjacent and transverse Cy5 **tBu-H** heterodimers templated by DNA Holliday junction (DNA HJ). The experimental absorption (upper figures) and circular dichroism (down figures) spectra (solid line) were converted into molar extinction coefficient units (ε $M^{-1}cm^{-1}$). Dot lines depict the modeled results using the Kühn−Renger−May approach (KRM model).

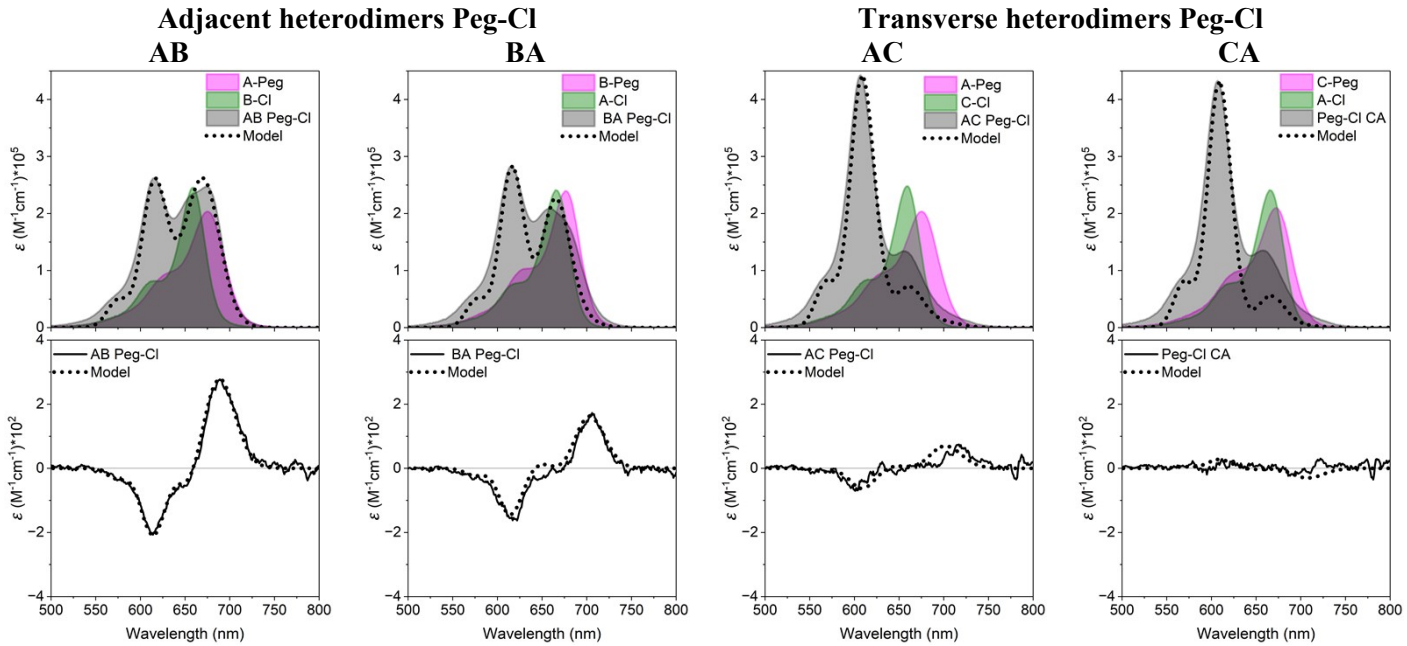

Figure S21. Optical characterization of adjacent and transverse Cy5 **Peg-Cl** heterodimers templated by DNA Holliday junction (DNA HJ). The experimental absorption (upper figures) and circular dichroism (down figures) spectra (solid line) were converted into molar extinction coefficient units (ε $M^{-1}cm^{-1}$). Dot lines depict the modeled results using the Kühn−Renger−May approach (KRM model).

SI-3.3. Peaks of heterodimers absoption spectra

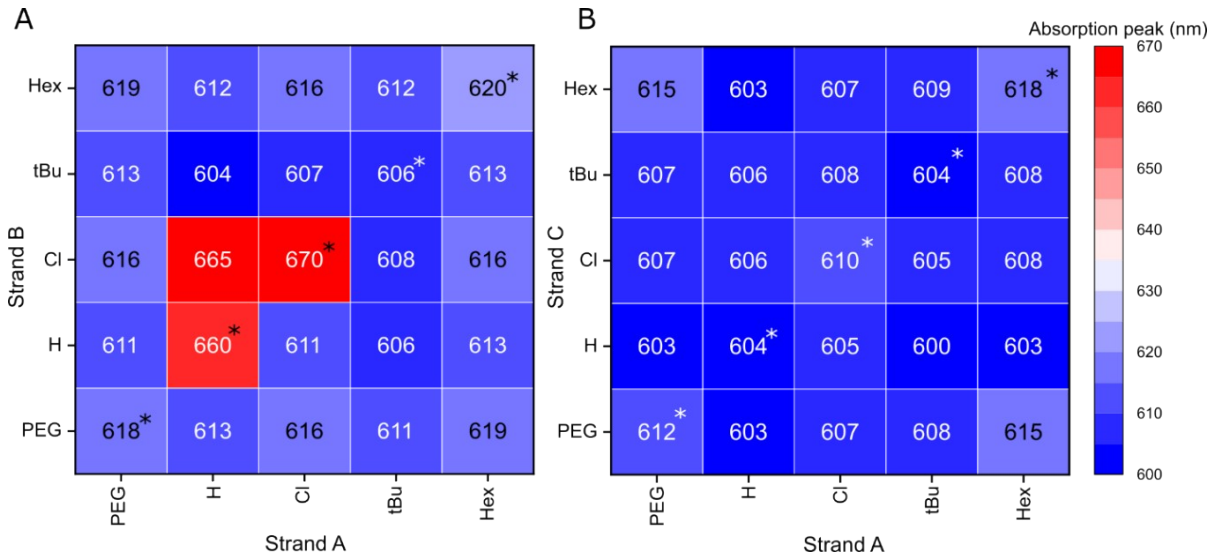

Figure S22. Maximum peak of absorption of adjacent [A] and transverse [B] homodimers(*data from 1) and heterodimers templated by DNA Holliday junction (DNA HJ).

SI-3.4. Circular dichroism spectra of Cy5 tBu-Cl

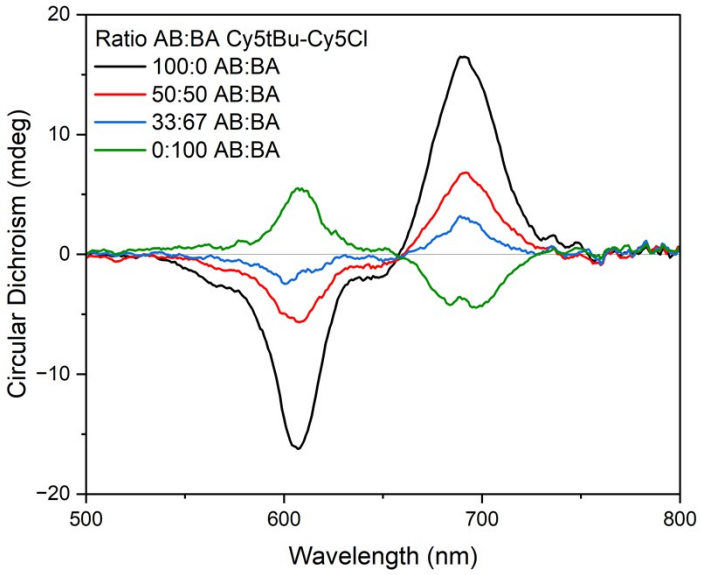

Figure S23. Circular dichroism profile of Cy5 tBu-Cl at different ratios of AB and BA heterodimers. Cy5 tBu-Cl AB exhibits stronger CD intensity than the BA heterodimer. This strong CD intensity was reduced by increasing the concentration of BA molar ratio on the solution, and the CD spectrum is inverted when there are no AB heterodimers. This inversion of the CD spectra may indicate the chiral inversion by changing the dye position from AB to BA.

SI-3.5. Fluorescence suppression

The fluorescence suppression of heterodimers in reference to their respective two monomers was calculated using the emission spectra scaled by the absorptance at the excited wavelength.

The florescence suppression of heterdimers was calculated using the integrated area of monomers ($\int FL_{\sum monomers})$ and dimers ($\int FL_{Xdimer})$ following formula[4]:

$$\%\, FL\ suppression = \frac{\int FL_{\sum Monomers} - \int FL_{Dimer}}{\int FL_{\sum Monomers}} x\ 100\%$$

Table S2. Fluorescence suppression (FL) in Cy5-R heterodimers

Dye position in DNA HJ	Area of dimer	∑Area monomers	FL (%)
BA	2.E+05	2.E+07	99
AB	4.E+05	2.E+07	98
AC	7.E+05	2.E+07	97
CA	2.E+05	2.E+07	99
AB	5.E+05	1.E+07	96
BA	5.E+05	2.E+07	97
AC	5.E+05	1.E+07	97
CA	7.E+05	2.E+07	96
AB	2.E+05	8.E+06	98
BA	4.E+05	8.E+06	95
AC	2.E+05	7.E+06	97
CA	3.E+05	8.E+06	96
AB	2.E+06	3.E+07	91
BA	2.E+06	3.E+07	94
AC	1.E+06	3.E+07	95
CA	2.E+06	3.E+07	94
AB	8.E+05	2.E+07	96
BA	9.E+05	2.E+07	95
AC	4.E+05	2.E+07	98
CA	4.E+05	2.E+07	98
AB	1.E+06	2.E+07	94
BA	1.E+06	2.E+07	94
AC	6.E+05	2.E+07	97
CA	7.E+05	2.E+07	96
AB	1.E+06	3.E+07	96
BA	9.E+05	3.E+07	97
AC	1.E+06	3.E+07	96
CA	1.E+06	3.E+07	96
AB	5.E+05	2.E+07	97
BA	3.E+05	2.E+07	98
AC	5.E+05	2.E+07	97
CA	5.E+05	2.E+07	98
AB	2.E+06	3.E+07	94
BA	2.E+06	3.E+07	92
AC	2.E+06	3.E+07	93
CA	1.E+06	4.E+07	97
AB	2.E+06	1.E+07	87
BA	2.E+06	2.E+07	89
AC	1.E+06	1.E+07	91
CA	1.E+06	2.E+07	90

SI-4. KRM modeling of heterodimers

Kühn, Renger, and May (KRM),[2] developed the theory extension of molecular exciton theory that includes vibronic coupling rather than only electronic coupling, and is sometimes called vibronic coupling theory. The KRM Model Simulation Tool simultaneously fits the absorption and circular dichroism (CD) spectra of aggregates to estimate the exciton hopping parameter $J_{m,n}$ and the specific orientation of transition dipole moments (TDM) of dyes. This specific orientation of TDMs is calculated using an interative stoichastic approach to populate and diagonalize a system Hamiltonian to predict theoretical absorption and circular dichroism spectra to compare with experimental data. See Roy *et al*.[3] for detailed information on the theoretical information and fitness metrics behind the homoaggregates KRM Model Simulation Tool.

Table S3. Key parameters estimated from absorption spectra of monomers in homo and heteroaggregates KRM modeling code.

Parameter	Units	Description	KRM Model Simulation Tool	
			Homoaggregate	Heteroaggregate
Energy of a vibron, ev[1]	eV	Energy spacing between vibrational states.	✓	✓
Displacements, d[1]	dimensionless	displacement of the excited harmonic oscillator potential from the ground-state potential.	✓	✓
Energy loss parameter, Γ[1]	eV	Half-width-at-half-max (HWHM) of 0-0 monomer transition	✓	✓[2]
Transition dipole moment, TDM	Debye	Transition dipole moment	X[3]	✓
Characteristic exciton hopping parameter, *J*0[1]	eV*nm^3	Constant pre-factor for calculation of exciton hopping parameter, $J_{m,n}$	✓	x
Energy of monomers, E0[1]	eV	Energy peak of monomer in the absorption spectrum	X[4]	✓
Length of dye, *l*	nm	Estimated length of dye	✓	✓

[1] Parameter calculated from the absorption spectra of monomers.
[2]Uses the average of two monomers. ✓ and X indicate the required and non-required data for each version of the KRM Model Simulation Tool, respectively.
[3]the KRM uses this value, which is calculated directly from the monomer spectrum and then used to calculate *J0*, but it is not a user input.
[4]It is not user input, the KRM simply uses the maximum values automatically

The heteroaggregate KRM Model Simulation Tool (version ev1HAv2, 2022) used in the present study and the homoaggregates KRM Model Simulation Tool used in previous studies[1,3–5] have the same theoretical formulation and operate similarly. Both versions of the simulation tool use key parameters of monomers (Table S24) to estimate the orientation of the TDM of dyes and $J_{m,n}$ of aggregates. The difference is that the heteroaggregate KRM Model Simulation Tool allows input of the characteristics of each monomer (*e.g.*, energy levels), enabling the estimation of the orientation TDM moment of different dyes and their $J_{m,n}$ in a heteroaggregate. Recently, Rolczynki *et al* 2024[6] presented an algorithm that has a similar approach to the KRM simulation tool to calculate the position and orientation of dyes in an aggregate and their electronic and vibrational transition energies.

In the simplest model of dipole coupling, monomers that are coupled have their monomer excited states split symmetrically into higher and lower energy states by $J_{m,n}$. In real systems, additional interactions between dyes and their surrounding environment can induce an energy shift in the monomer that breaks the symmetry of ideal Davidov splitting.[7] The effect is captured in the KRM Simulation tool with an empirical fitting parameter, E_{off}, representing this energy offset (Figure S24). When there are sufficient spectral markers (*e.g.*, well defined peaks in absorption and CD), the E_{off} fitting parameter is adjusted by the user to align peak positions while considering both absorption and CD spectra of the aggregate. Thus, the predicted spectra and observed absorption and CD spectra features are aligned using either homo or heteroaggregate KRM Model Simulation Tools. Physically, E_{off} captures all dye-dye interaction (*e.g.*, van de Waals interaction) bot the interaction of the transition dipole moments (TDM).

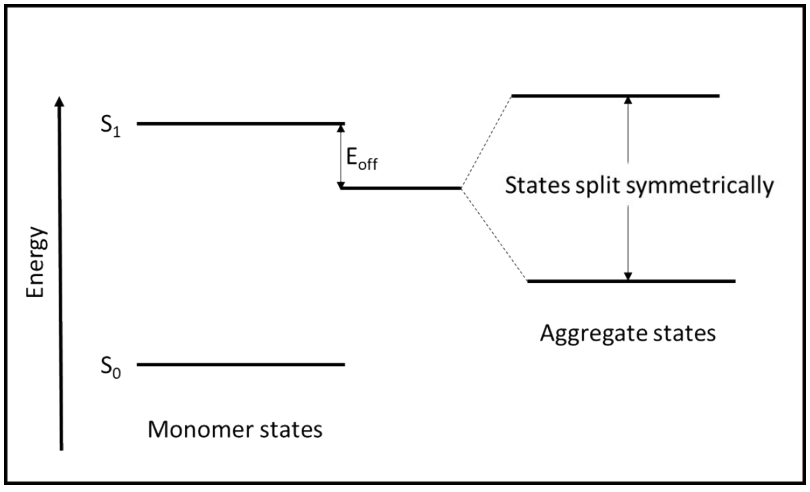

Figure S24. Effect of the offset energy (E_{off}) on the alignment of monomers at the excited state. The E_{off} value can be positive or negative. Scheme modified from Kasha *et al.*[8]

Modeling dimer with single and multiple populations in a sample

Initially, all samples of dimers are models as they have one type of dimer using a pair of TDM vectors (single population of dimer). The simulation tool calculates $J_{m,n}$ and the packing geometry of dyes using the key parameter of monomers, absorption and CD spectra of dimers and adjusting the E_{off} fitting parameter. If the normalized overlap integral of the experimental and theoretical absorption and CD is high (*e.g.*>90%), the sample is assigned as it has a single dimer population. However, if the normalized overlap integral of the experimental and theoretical absorption and CD is low (*e.g.*<90%), we proceeded to model as in the sample there are two types of dimers (dimer with subpopulation or mixture of dimers).[4] The approach of two dimers in the same sample uses two pairs of TDM vectors with the same characteristics of monomers used in a modeling of single population of dimer. The distance between each pair of vectors is set to 1 μm to ensure zero $J_{m,n}$ between the two types of dimers. Other modeling parameters are the same as those used to model one type of dimer in a sample. The final result is given based on the best fit comparing the experimental and predicted absoption and CD spectra of one type and two types of dimers population modeling results.

SI-4.1. 3D plots of transition dipole moments of dyes in adjacent and transverse heterodimers

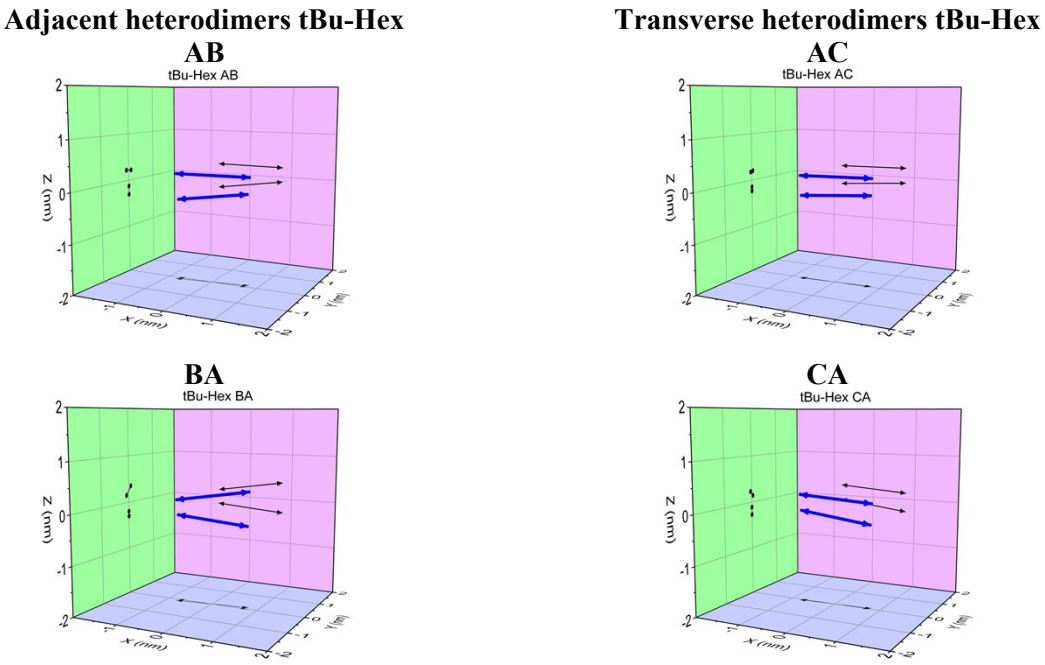

Figure S25. 3D plot of transition dipole moments (TDM) of Cy5 tBu-Hex heterodimers (blue arrows) projected to XY, YZ, and XZ planes (black arrows) derived from KRM modeling.

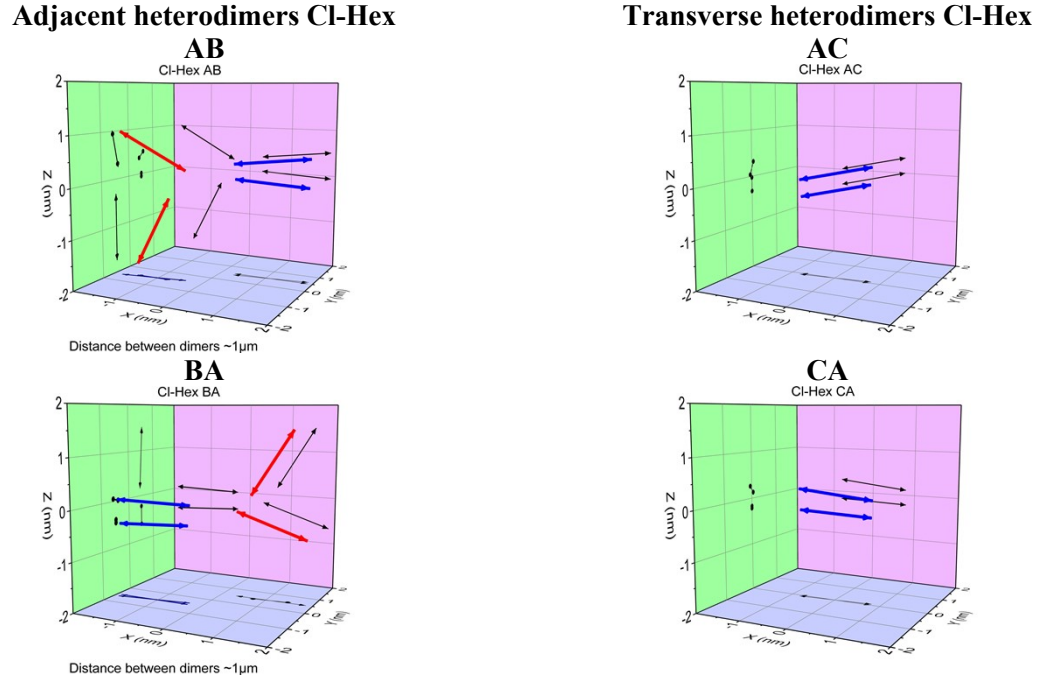

Figure S26. 3D plot of transition dipole moments (TDM) of Cy5 Cl-Hex heterodimers (blue and red arrows) projected to XY, YZ, and XZ planes (black arrows) derived from KRM modeling.

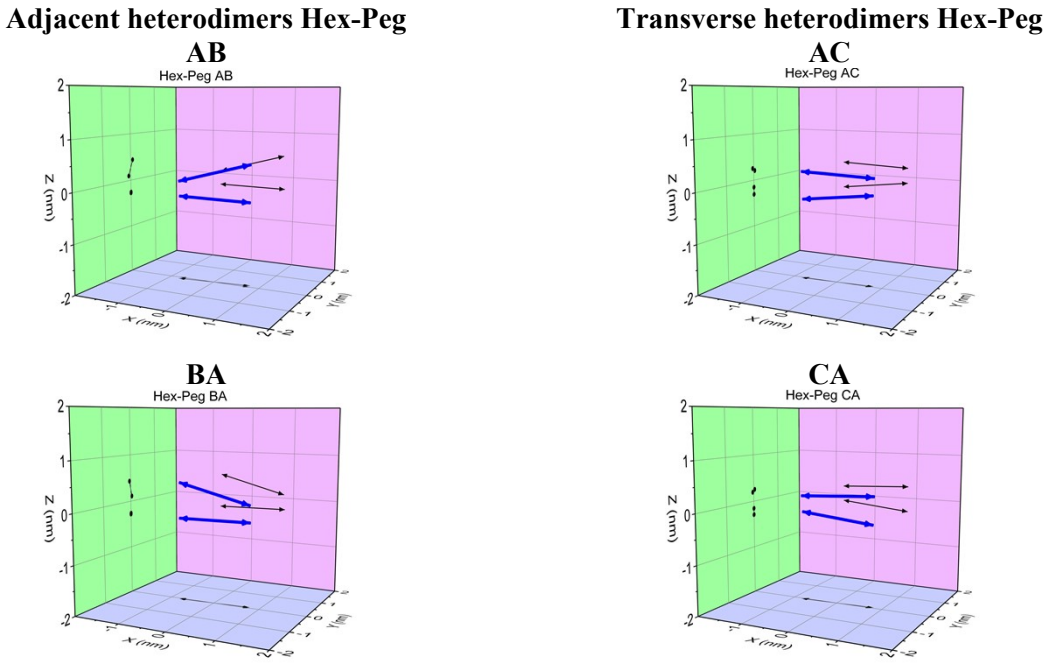

Figure S27. 3D plot of transition dipole moments (TDM) of Cy5 Hex-Peg heterodimers (blue arrows) projected to XY, YZ, and XZ planes (black arrows) derived from KRM modeling.

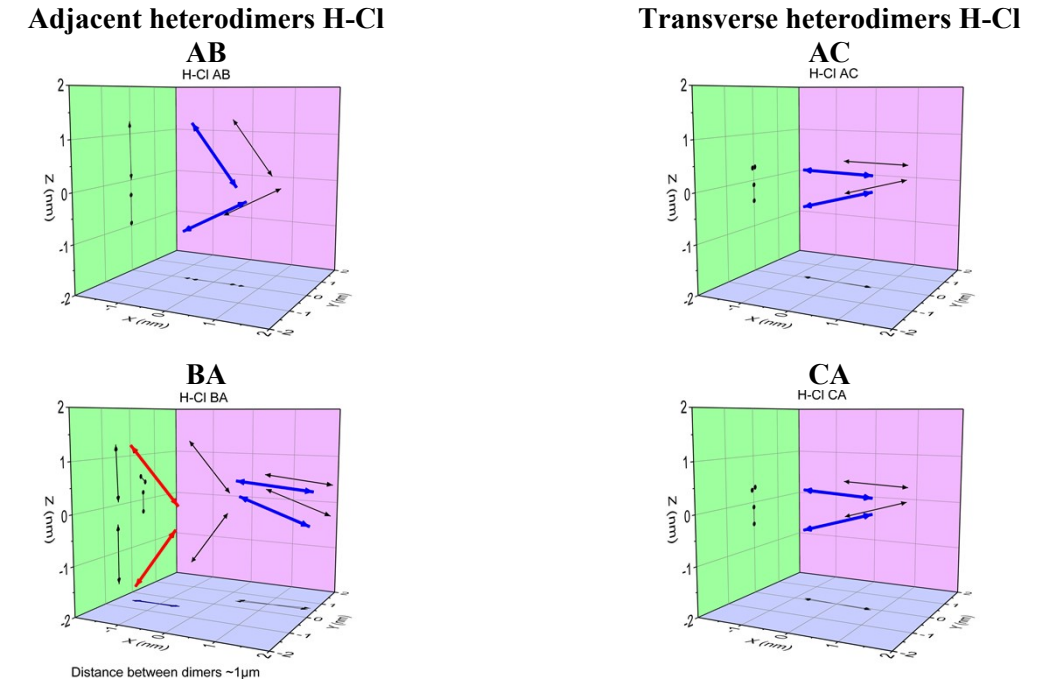

Figure S28. 3D plot of transition dipole moments (TDM) of Cy5 H-Cl heterodimers (blue and red arrows) projected to XY, YZ, and XZ planes (black arrows) derived from KRM modeling.

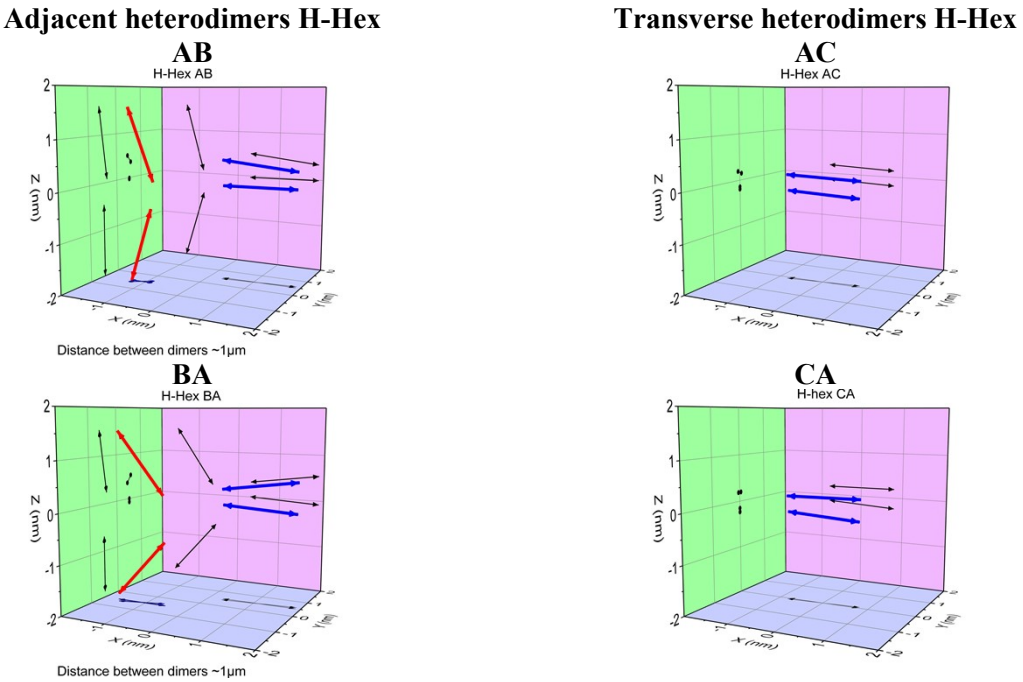

Figure S29. 3D plot of transition dipole moments (TDM) of Cy5 H-Hex heterodimers (blue and red arrows) projected to XY, YZ, and XZ planes (black arrows) derived from KRM modeling.

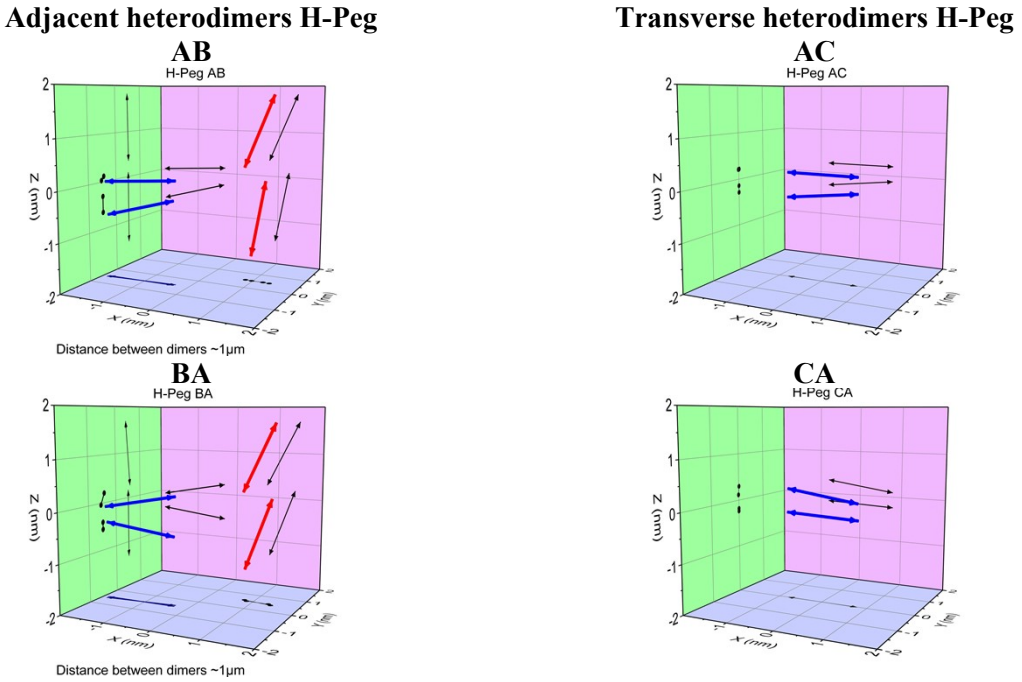

Figure S30. 3D plot of transition dipole moments (TDM) of Cy5 **H-Peg** heterodimers (blue and red arrows) projected to XY, YZ, and XZ planes (black arrows) derived from KRM modeling.

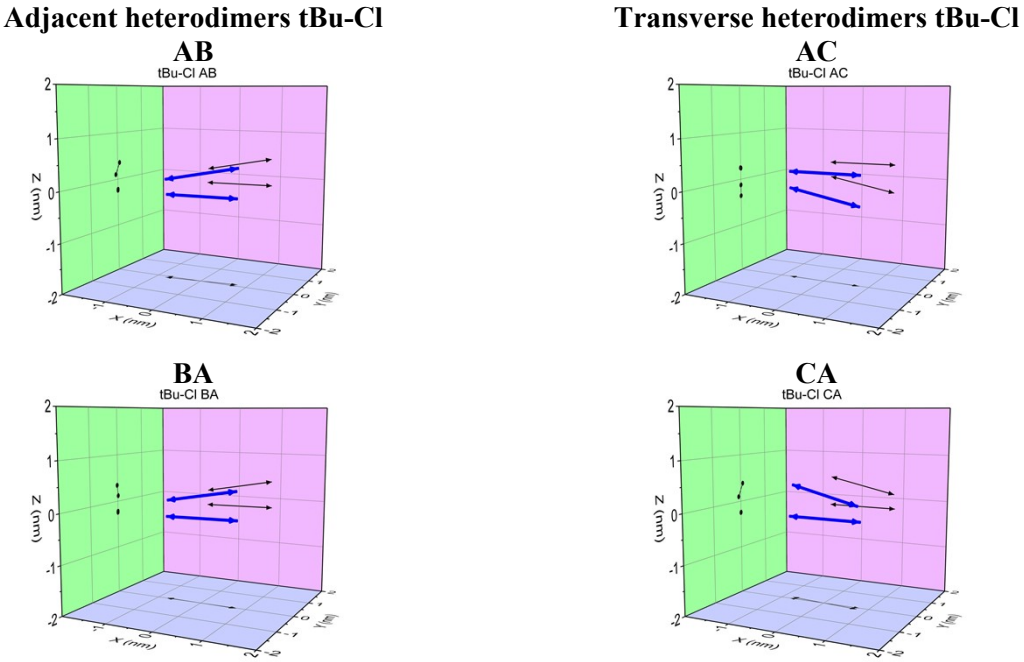

Figure S31. 3D plot of transition dipole moments (TDM) of Cy5 tBu-Cl heterodimers (blue arrows) projected to XY, YZ, and XZ planes (black arrows) derived from KRM modeling.

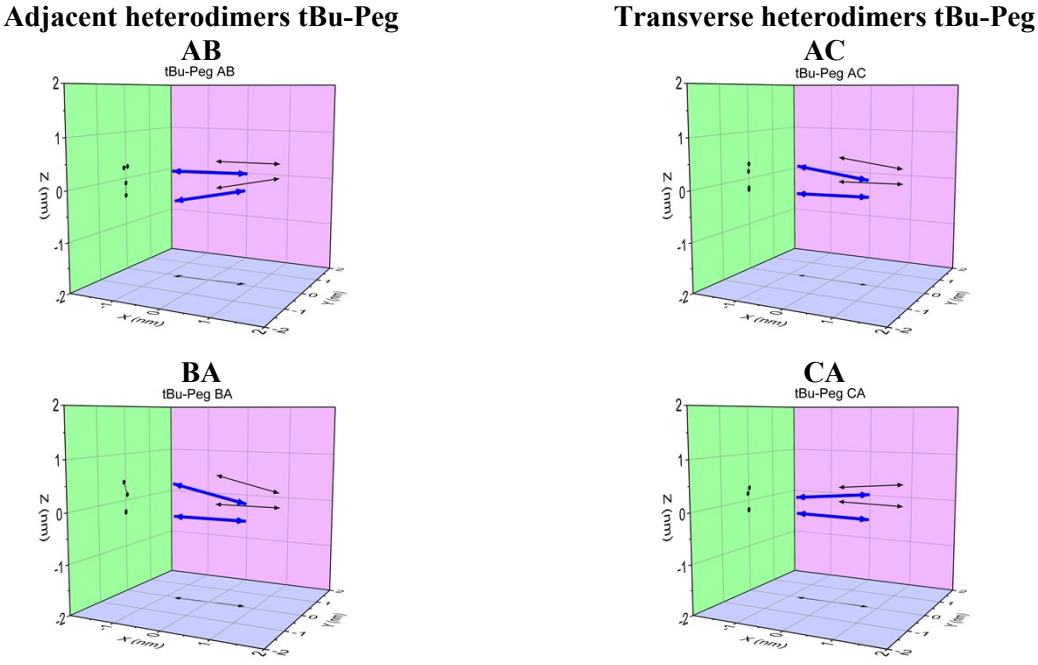

Figure S32. 3D plot of transition dipole moments (TDM) of Cy5 tBu-Peg heterodimers (blue arrows) projected to XY, YZ, and XZ planes (black arrows) derived from KRM modeling.

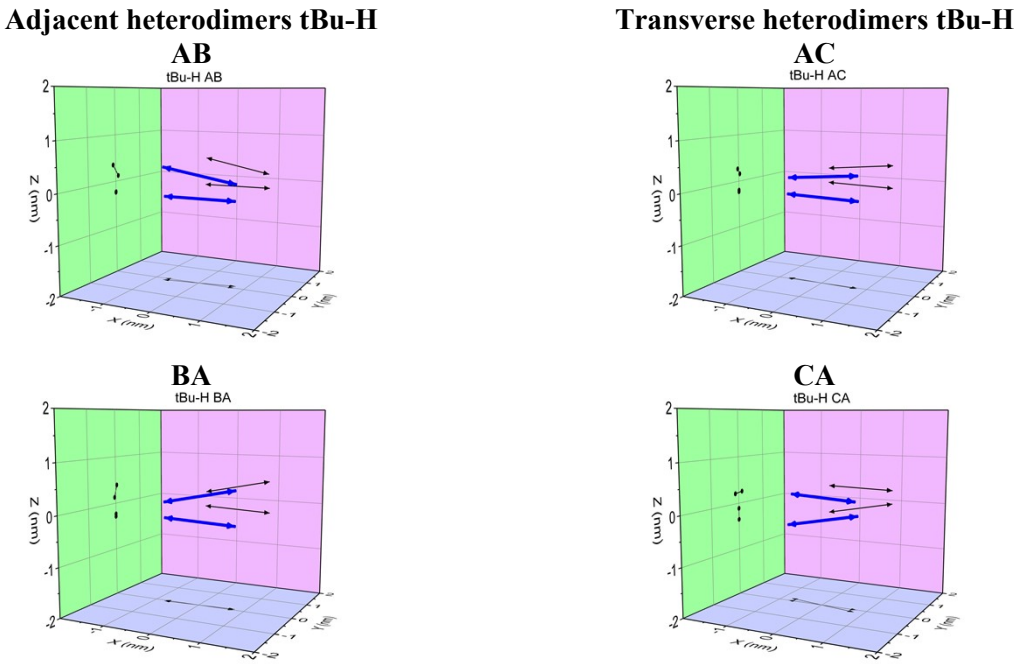

Figure S33. 3D plot of transition dipole moments (TDM) of Cy5 tBu-H heterodimers (blue arrows) projected to XY, YZ, and XZ planes (black arrows) derived from KRM modeling.

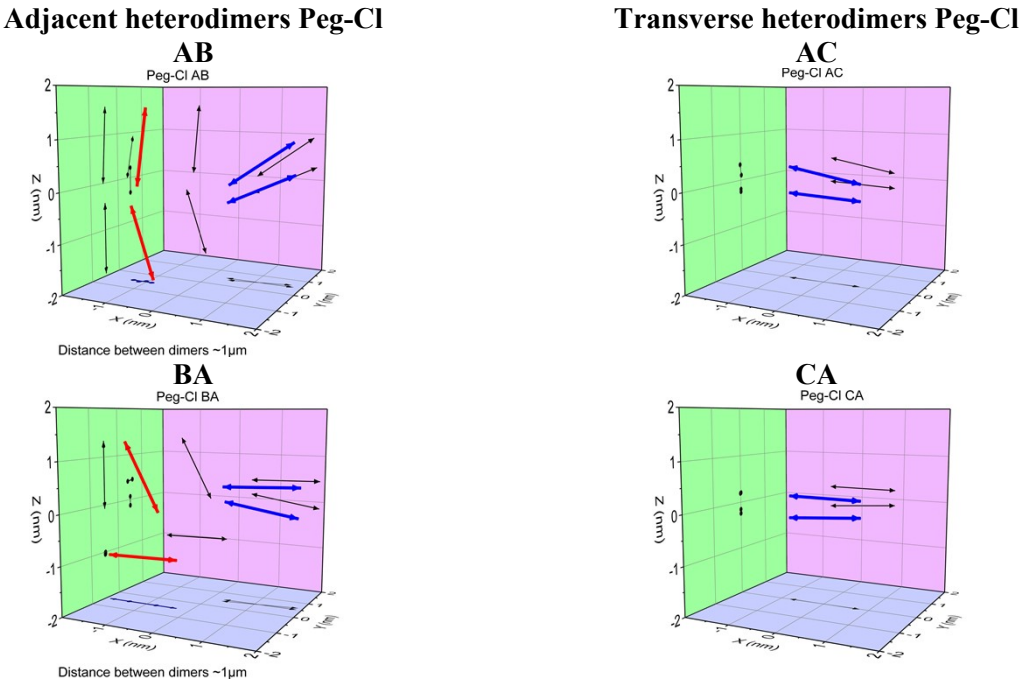

Figure S34. 3D plot of transition dipole moments (TDM) of Cy5 Peg-Cl heterodimers (blue arrows) projected to XY, YZ, and XZ planes (black arrows) derived from KRM modeling.

SI-4.2. Input and output parameters of KRM of Adjacent AB and transverse AC heterodimers

List of parameters used in KRM modeling:

Ev - The energy of vibron (*eV*)

d - Displacement of excited state vibronic potential (dimensionless units)

Γ - Energy loss damping constant (*eV*)

J_0 - Characteristic exchange energy ($meV\text{-}nm^3$)

E_0 - The energy at which the monomer absorption peak is located (eV).

M - Dipole Moment (*Debye*)

nv - Vibrational state Hilbert space

E_{off} - Energy offset from monomer (*meV*)

l - Length of the transition dipole moment (*nm*)

cdis - Closest distance between the long axes of any pair of dyes (*nm*)

r - The ratio of theoretical to experimental values of the ratio of the max abs CD peak height to max absorbance peak height

OI_{AB} - Normalized overlap integral for the experimental and theoretical absorbance curves

OI_{CD} - Normalized overlap integral for the experimental and theoretical CD spectra

OI_{Tot} - Mean of OI_{AB} and OI_{CD}

MSD_{abs} - Absorbance spectrum mean-square deviation

MSD_{cd} - CD spectrum mean-square deviation

$w_{abscd}rms$ - Weighted mean-squared deviation between the experimental and theoretical ABS and CD spectra

$J_{m,n}$ – The excitonic hopping parameter (*meV*)

R - Center-to-Center distance (Å)

dmin - The shortest distance between the transition dipole moment vectors (*nm*)

α - angle between transition dipole moments (TDM) of dyes (°)

θ_{1s} - Slip angle, the angle between dye 1 and the line connecting dye centers (°)

θ_{2s} - Slip angle, the angle between dye 2 and the line connecting dye centers (°)

θ_t - Twist angle, the angle between dye 1 and dye 2 in the XY plane (rotation about Z-axis or R) (°)

SI-4.2.1. Monomers

Table S4. Parameters of monomer Cy5-R

Dye (Cy5-R)	Position in DNA-HJ	E_v (eV)	*d* (dimensionless)	Γ (eV)	E_0 (eV)	M (Debye)	*l* (nm)
Cy5 Peg	A	0.142	0.935	0.049	1.84	14.2	1.4
	B	0.136	0.925	0.042	1.83	14.5	1.4
	C	0.139	0.950	0.045	1.84	14.2	1.4
	D	0.144	0.920	0.053	1.85	13.9	1.4
Cy5 Cl	A	0.132	0.795	0.040	1.86	13.4	1.4
	B	0.135	0.815	0.037	1.88	13.5	1.4
	C	0.136	0.815	0.039	1.88	13.7	1.4
	D	0.142	0.830	0.043	1.87	13.2	1.4
Cy5 tBu	A	0.137	0.860	0.045	1.87	13.7	1.4
	B	0.136	0.870	0.043	1.88	13.9	1.4
	C	0.136	0.830	0.038	1.88	12.9	1.4
	D	0.138	0.850	0.042	1.88	12.9	1.4
Cy5 H	A	0.137	0.820	0.040	1.90	12.8	1.4
	B	0.133	0.810	0.037	1.90	12.9	1.4
	C	0.135	0.800	0.039	1.91	13.1	1.4
	D	0.140	0.820	0.043	1.90	13.0	1.4
Cy5 Hex	A	0.140	0.970	0.051	1.82	14.2	1.4
	B	0.137	0.945	0.043	1.82	13.9	1.4
	C	0.140	0.968	0.048	1.83	13.3	1.4

SI-4.2.2. Adjacent AB heterodimers

Table S5. Input fitting parameters used in calculation of adjacent AB and BA heterodimers

Heterodimer	Position in DNA-HJ	# dyes*	nv	E_{off} (meV)	Γ (eV)	c_{dis} (nm)
Hex-tBu	AB	2	3	10	0.05	0.34
	BA	2	3	10	0.04	0.34
Hex-Cl	AB	4	3	10	0.04	0.34
	BA	4	3	10	0.04	0.34
Hex-Peg	AB	2	3	10	0.05	0.34
	BA	2	3	10	0.05	0.34
H-Cl	AB	2	3	10	0.04	0.34
	BA	4	3	10	0.04	0.34
H-Hex	AB	4	3	10	0.04	0.34
	BA	4	3	10	0.04	0.34
H-Peg	AB	4	3	10	0.04	0.34
	BA	4	3	10	0.04	0.34
tBu-Cl	AB	2	3	10	0.04	0.34
	BA	2	3	10	0.04	0.34
tBu-Peg	AB	2	3	10	0.04	0.34
	BA	2	3	10	0.05	0.34
Peg-Cl	AB	4	3	10	0.04	0.34
	BA	4	3	10	0.04	0.34
tBu-H	AB	2	3	10	0.04	0.34
	BA	2	3	10	0.04	0.34

*Four chromophores were used to fit only dimer with subpopulations (*e.g.* mixture of J- and H-like aggregates).

Table S6. Hopping parameter ($J_{m,n}$) and geometric parameters of dyes in adjacent AB and BA heterodimers

Heterodimer	Position in DNA-HJ	$J_{m,n}$ (meV)	$R_{m,n}$ (nm)	$dmin_{m,n}$ (nm)	Θ_{1s} (°)	Θ_{2s} (°)	Θ_t (°)	$\alpha_{m,n}$ (°)
Hex-tBu	AB	104	0.50	0.34	85	82	7	15
	BA	113	0.44	0.34	82	90	8	11
Hex-Cl	AB*	35	1.28	0.45	73	33	7	75
		103	0.45	0.41	87	88	8	9
	BA*	108	0.45	0.34	87	84	7	11
		20	1.66	0.67	28	62	8	89
Hex-Peg	AB	103	0.54	0.34	89	75	7	17
	BA	98	0.54	0.34	89	76	4	16
Cl-H	AB	47	1.27	0.34	63	38	2	79
	BA*	88	0.51	0.34	71	84	8	15
		28	1.71	0.48	37	42	3	79
H-Hex	AB*	104	0.44	0.35	89	84	6	9
		22	2.06	0.55	17	18	29	34
	BA*	100	0.48	0.35	87	83	6	12
		12	2.17	0.95	43	36	14	78
H-Peg	AB*	-29	1.78	0.53	11	23	-3	13
		83	0.55	0.40	75	87	4	12
	BA*	-21	1.55	0.63	21	28	-11	8
		87	0.57	0.34	84	80	5	17
tBu-Cl	AB	105	0.46	0.34	89	79	7	12
	BA	107	0.46	0.34	89	80	-1	9
tBu-Peg	AB	109	0.48	0.34	78	89	6	13
Peg-tBu	BA	103	0.51	0.34	89	78	5	14
Peg-Cl	AB*	86	0.52	0.35	66	56	11	14
		30	1.97	0.46	19	7	38	24
	BA*	110	0.46	0.34	81	89	8	13
		10	1.66	0.94	89	29	0	63
tBu-H	AB	98	0.47	0.34	90	79	9	14
	BA	92	0.52	0.34	88	79	4	14

* Modeling results of dimer with subpopulations; data exhibiting the higher $J_{m,n}$ value was used for calculation of dyes properties on exciton delocalization described in the main text.

$J_{m,n}$ was calculated fitting the circular dichroism and absorption spectra and parameters calculated for monomers. Γ (eV) for dimers modeling was the average between the two participant dyes.

Table S7. Coordinates of dyes describing each dye orientation and position in adjacent AB and BA heterodimers.

Heterodimer	Position in DNA-HJ	Dye 1					Dye 2				
		Θ_m (°)	Φ_m (°)	x_m (nm)	y_m (nm)	z_m (nm)	Θ_n (°)	Φ_n (°)	x_n (nm)	y_n (nm)	z_n (nm)
Hex-tBu	AB	95	0	0.00	0.00	-0.25	82	7	0.00	0.00	0.25
	BA	82	0	0.00	0.00	-0.22	90	8	0.00	0.00	0.22
Hex-Cl	AB*	107	0	0.00	0.00	-0.64	33	7	0.00	0.00	0.64
		87	0	0.00	0.00	-0.23	92	8	0.00	0.00	0.23
	BA*	93	0	0.00	0.00	-0.22	84	7	0.00	0.00	0.22
		28	0	0.00	0.00	-0.83	118	8	0.00	0.00	0.83
Hex-Peg	AB	91	0	0.00	0.00	-0.27	75	7	0.00	0.00	0.27
	BA	89	0	0.00	0.00	-0.27	104	4	0.00	0.00	0.27
Cl-H	AB	63	0	0.00	0.00	-0.63	142	2	0.00	0.00	0.63
	BA*	109	0	0.00	0.00	-0.25	96	8	0.00	0.00	0.25
		37	0	0.00	0.00	-0.86	138	3	0.00	0.00	0.86
H-Hex	AB*	89	0	0.00	0.00	-0.22	96	6	0.00	0.00	0.22
		17	0	0.00	0.00	-1.03	162	29	0.00	0.00	1.03
	BA*	93	0	0.00	0.00	-0.24	83	6	0.00	0.00	0.24
		43	0	0.00	0.00	-1.08	144	14	0.00	0.00	1.08
H-Peg	AB*	11	0	0.00	0.00	-0.89	23	-3	0.00	0.00	0.89
		75	0	0.00	0.00	-0.28	87	4	0.00	0.00	0.28
	BA*	21	0	0.00	0.00	-0.78	28	-11	0.00	0.00	0.78
		96	0	0.00	0.00	-0.28	80	5	0.00	0.00	0.28
tBu-Cl	AB	89	0	0.00	0.00	-0.23	79	7	0.00	0.00	0.23
	BA	89	0	0.00	0.00	-0.23	80	-1	0.00	0.00	0.23
tBu-Peg	AB	78	0	0.00	0.00	-0.24	89	6	0.00	0.00	0.24
Peg-tBu	BA	89	0	0.00	0.00	-0.26	102	5	0.00	0.00	0.26
Peg-Cl	AB*	66	0	0.00	0.00	-0.26	56	11	0.00	0.00	0.26
		161	0	0.00	0.00	-0.99	7	38	0.00	0.00	0.99
	BA*	99	0	0.00	0.00	-0.23	89	8	0.00	0.00	0.23
		89	0	0.00	0.00	-0.83	151	0	0.00	0.00	0.83
tBu-H	AB	90	0	0.00	0.00	-0.24	101	9	0.00	0.00	0.24
	BA	92	0	0.00	0.00	-0.26	79	4	0.00	0.00	0.26

* Modeling results of dimer with subpopulations, the distance between dimers is ~1,000 nm. Data exhibiting the higher $J_{m,n}$ value was used for calculation of dye properties on exciton delocalization described in the main text.

Data depict standard orientation and position of dimers.

Table S8. Goodness of fit and fit weight of adjacent AB Cy5-R heterodimers

Heterodimer	Position in DNA-HJ	Goodness of fit results						Goodness of fit weight						W_{absCD}rms
		rr	OI_{abs}	OI_{CD}	OI_{total}	MSD_{ABS}	MSD_{CD}	rr	OI_{abs}	OI_{CD}	OI_{total}	MSD_{ABS}	MSD_{CD}	
Hex-tBu	AB	1.00	0.99	0.98	0.99	0.12	0.53	1	0	0	n/a	1	1	0.64
	BA	1.00	0.99	0.97	0.98	0.19	0.70	1	0	0	n/a	1	1	0.89
Hex-Cl	AB	0.99	1.00	0.97	0.98	0.06	0.70	1	0	0	n/a	1	1	0.76
	BA	1.03	0.99	0.95	0.97	0.33	1.19	1	0	0	n/a	1	1	1.53
Hex-Peg	AB	1.00	0.99	0.98	0.98	0.18	0.45	1	0	0	n/a	1	1	0.63
	BA	1.01	0.93	0.96	0.95	1.74	0.75	1	0	0	n/a	1	1	2.49
H-Cl	AB	0.98	0.99	0.92	0.95	0.30	1.00	1	0	0	n/a	1	0	0.30
	BA	0.97	0.99	0.98	0.98	0.66	0.33	1	0	0	n/a	1	1	0.99
H-Hex	AB	1.00	0.99	0.98	0.99	0.34	0.76	1	0	0	n/a	1	1	1.10
	BA	1.02	1.00	0.97	0.99	0.10	0.69	1	0	0	n/a	1	1	0.78
H-Peg	AB	1.00	0.99	0.87	0.93	0.44	2.56	1	0	0	n/a	5	1	4.78
	BA	0.99	0.99	0.99	0.99	0.36	0.22	1	0	0	n/a	1	1	0.58
tBu-Cl	AB	1.01	0.95	0.96	0.96	0.88	0.68	1	0	0	n/a	1	5	4.26
	BA	1.00	0.97	0.90	0.94	0.39	1.92	1	0	0	n/a	1	0	0.39
tBu-Peg	AB	1.01	0.98	0.96	0.97	0.29	0.81	1	0	0	n/a	1	1	1.10
	BA	1.00	0.99	0.94	0.96	0.11	1.28	1	0	0	n/a	1	1	1.39
Peg-Cl	AB	0.99	0.99	0.99	0.99	0.27	0.12	1	0	0	n/a	1	1	0.39
	BA	1.07	0.98	0.97	0.97	0.57	0.64	1	0	0	n/a	1	1	1.21
tBu-H	AB	1.03	0.97	0.98	0.98	0.61	0.36	1	0	0	n/a	1	1	0.96
	BA	1.00	0.96	0.95	0.95	0.86	0.94	1	0	0	n/a	1	1	1.80

SI-4.2.3. Transverse AC heterodimers

Table S9. Input fitting parameters used in calculation of transverse AC and CA heterodimers

Heterodimer	Position in DNA-HJ	# dyes	nv	E_{off} (meV)	Γ (eV)	c_{dis} (nm)
Hex-tBu	AC	2	3	10	0.04	0.34
	CA	2	3	10	0.05	0.34
Hex-Cl	AC	2	3	10	0.05	0.34
	CA	2	3	10	0.04	0.34
Hex-Peg	AC	2	3	10	0.05	0.34
	CA	2	3	10	0.05	0.34
H-Cl	AC	2	3	15	0.04	0.34
	CA	2	3	15	0.04	0.34
H-Hex	AC	2	3	10	0.04	0.34
	CA	2	3	10	0.05	0.34
H-Peg	AC	2	3	10	0.04	0.34
	CA	2	3	10	0.04	0.34
tBu-Cl	AC	2	3	10	0.04	0.34
	CA	2	3	10	0.04	0.34
tBu-Peg	AC	2	3	10	0.05	0.34
	CA	2	3	10	0.04	0.34
Peg-Cl	AC	2	3	10	0.04	0.34
	CA	2	3	10	0.04	0.34
tBu-H	AC	2	3	10	0.04	0.34
	CA	2	3	10	0.04	0.34

Table S10. Hopping parameter ($J_{m,n}$) and geometric parameters of dyes in transverse AC and CA heterodimers

Heterodimer	Position in DNA-HJ	$J_{m,n}$ (meV)	$R_{m,n}$ (nm)	$dmin_{m,n}$ (nm)	Θ_{1s} (°)	Θ_{2s} (°)	Θ_t (°)	$\alpha_{m,n}$ (°)
Hex-tBu	AC	129	0.38	0.34	83	86	4	5
	CA	127	0.38	0.34	86	89	3	5
Hex-Cl	AC	132	0.39	0.34	88	84	5	6
	CA	133	0.35	0.34	77	78	6	6
Hex-Peg	AC	115	0.46	0.34	83	88	3	10
	CA	110	0.45	0.34	84	88	3	9
H-Cl	AC	86	0.55	0.34	75	89	-4	16
	CA	82	0.58	0.34	74	88	-5	19
H-Hex	AC	133	0.34	0.34	88	88	6	6
	CA	127	0.39	0.34	86	90	4	5
H-Peg	AC	112	0.43	0.34	84	90	-1	7
	CA	118	0.42	0.34	88	82	-1	6
tBu-Cl	AC	103	0.49	0.34	80	90	-1	11
	CA	101	0.49	0.34	90	78	-7	14
tBu-Peg	AC	113	0.46	0.34	88	83	-1	8
	CA	117	0.42	0.34	90	85	2	6
Peg-Cl	AC	116	0.44	0.34	88	80	2	8
	CA	127	0.40	0.34	86	90	-1	4
tBu-H	AC	112	0.43	0.34	89	85	-3	7
	CA	92	0.47	0.34	80	89	-11	16

$J_{m,n}$ was calculated fitting the circular dichroism and absorption spectra and parameters calculated for monomers. Γ (eV) for dimers modeling was the average between the two participant dyes.

Table S11. Coordinates of dyes describing each dye orientation and position in transverse AC and CA heterodimers.

Heterodimer	Position in DNA-HJ	Dye 1					Dye 2				
		Θ_m (°)	Φ_m (°)	x_m (nm)	y_m (nm)	z_m (nm)	Θ_n (°)	Φ_n (°)	x_n (nm)	y_n (nm)	z_n (nm)
Hex-tBu	AC	97	0	0.00	0.00	-0.19	94	4	0.00	0.00	0.19
	CA	86	0	0.00	0.00	-0.19	89	3	0.00	0.00	0.19
Hex-Cl	AC	92	0	0.00	0.00	-0.20	96	5	0.00	0.00	0.20
	CA	77	0	0.00	0.00	-0.18	78	6	0.00	0.00	0.18
hex-Peg	AC	83	0	0.00	0.00	-0.23	92	3	0.00	0.00	0.23
	CA	96	0	0.00	0.00	-0.23	88	3	0.00	0.00	0.23
H-Cl	AC	75	0	0.00	0.00	-0.28	91	-4	0.00	0.00	0.28
	CA	74	0	0.00	0.00	-0.29	92	-5	0.00	0.00	0.29
H-Hex	AC	92	0	0.00	0.00	-0.17	92	6	0.00	0.00	0.17
	CA	94	0	0.00	0.00	-0.19	90	4	0.00	0.00	0.19
H-Peg	AC	84	0	0.00	0.00	-0.21	90	-1	0.00	0.00	0.21
	CA	92	0	0.00	0.00	-0.21	98	-1	0.00	0.00	0.21
tBu-Cl	AC	100	0	0.00	0.00	-0.24	90	-1	0.00	0.00	0.24
	CA	90	0	0.00	0.00	-0.24	102	-7	0.00	0.00	0.24
tBu-Peg	AC	88	0	0.00	0.00	-0.23	97	-1	0.00	0.00	0.23
	CA	90	0	0.00	0.00	-0.21	85	2	0.00	0.00	0.21
Peg-Cl	AC	92	0	0.00	0.00	-0.22	100	2	0.00	0.00	0.22
	CA	86	0	0.00	0.00	-0.20	90	-1	0.00	0.00	0.20
tBu-H	AC	91	0	0.00	0.00	-0.21	85	-3	0.00	0.00	0.21
	CA	80	0	0.00	0.00	-0.23	91	-11	0.00	0.00	0.23

Data depict the standard orientation and position of dimers.

Table S12. Goodness of fit and fit weight of transverse AC Cy5-R heterodimers

Heterodimer	Position in DNA-HJ	Goodness of fit results						Goodness of fit weight						W_{absCD}rms
		rr	OI_{abs}	OI_{CD}	OI_{total}	MSD_{ABS}	MSD_{CD}	rr	OI_{abs}	OI_{CD}	OI_{total}	MSD_{ABS}	MSD_{CD}	
Hex-tBu	AC	0.99	0.98	0.98	0.98	0.27	0.53	1.0	0	0	n/a	1	1	0.81
	CA	1.00	0.99	0.92	0.95	0.25	1.81	1.0	0	0	n/a	1	1	2.07
Hex-Cl	AC	1.01	0.99	0.98	0.98	0.14	0.63	1.0	0	0	n/a	1	1	0.77
	CA	1.00	0.98	0.94	0.96	0.25	1.37	1.0	0	0	n/a	1	1	1.62
hex-Peg	AC	1.00	0.99	0.95	0.97	0.12	1.36	1.0	0	0	n/a	1	0	0.12
	CA	1.00	0.99	0.85	0.92	0.10	3.20	1.0	0	0	n/a	1	0	0.10
H-Cl	AC	1.01	0.97	0.95	0.96	0.64	0.89	1.0	0	0	n/a	1	1	1.53
	CA	1.00	0.97	0.97	0.97	0.64	0.79	1.0	0	0	n/a	1	1	1.43
H-hex	AC	0.99	0.99	0.93	0.96	0.16	1.65	1.0	0	0	n/a	1	1	1.81
	CA	1.01	0.99	0.97	0.98	0.15	1.00	1.0	0	0	n/a	1	1	1.15
H-Peg	AC	0.99	0.98	0.84	0.91	0.42	3.19	1.0	0	0	n/a	1	1	3.61
	CA	1.00	0.98	0.47	0.72	0.33	10.32	1.0	0	0	n/a	1	0	0.33
tBu-Cl	AC	1.00	0.98	0.04	0.51	0.42	15.63	1.0	0	0	n/a	1	0	0.42
	CA	1.02	0.97	0.97	0.97	0.62	0.66	1.0	0	0	n/a	1	0	0.62
tBu-Peg	AC	1.00	0.98	0.17	0.58	0.32	21.33	1.0	0	0	n/a	1	0	0.32
	CA	1.00	0.98	0.38	0.68	0.33	10.29	1.0	0	0	n/a	1	0	0.33
Peg-Cl	AC	1.00	0.98	0.78	0.88	0.34	4.27	1.0	0	0	n/a	1	0	0.34
	CA	1.00	0.97	0.24	0.60	0.58	14.23	1.0	0	0	n/a	1	0	0.58
tBu-H	AC	1.00	0.96	0.97	0.96	0.89	0.62	1.0	0	0	n/a	1	1	1.51
	CA	1.02	0.98	0.98	0.98	0.52	0.33	1.0	0	0	n/a	1	1	0.85

SI-4.3. Input and output parameters of KRM of additional heterodimers

SI-4.3.1. KRM results of Cy5 tBu-H

Table S13. Parameters of monomer Cy5-tBu and Cy5-H

Dye	Position in DNA-HJ	E_v (eV)	*d* (dimensionless)	Γ (eV)	E0 (eV)	M (Debye)	*l* (nm)
Cy5 tBu	A	0.137	0.860	0.045	1.87	13.7	1.4
	B	0.136	0.870	0.043	1.88	13.9	1.4
	C	0.136	0.830	0.038	1.88	12.9	1.4
	D	0.138	0.850	0.042	1.88	12.9	1.4
Cy5 H	A	0.137	0.820	0.040	1.90	12.8	1.4
	B	0.133	0.810	0.037	1.90	12.9	1.4
	C	0.135	0.800	0.039	1.91	13.1	1.4
	D	0.140	0.820	0.043	1.90	13.0	1.4

Table S14. Input fitting parameters used in calculation Cy5 tBu-H heterodimers.

Heterodimer Cy5 tBu-H	Position in DNA HJ	#Dyes*	nv	E_{off} (meV)	Γ (eV)	c_{dis} (nm)
Adjacent dimers	AB	2	3	10	0.041	0.34
	BA	2	3	10	0.042	0.34
	BC	4	3	10	0.041	0.34
	CB	4	3	10	0.038	0.34
	CD	4	3	10	0.041	0.34
	DC	4	3	10	0.041	0.34
	AD	2	3	10	0.044	0.34
	DA	2	3	10	0.041	0.34
Transverse dimers	AC	2	3	10	0.042	0.34
	CA	2	3	10	0.039	0.34
	BD	2	3	10	0.043	0.34
	DB	2	3	10	0.040	0.34

*Four chromophores were used to fit only dimer with subpopulations (*e.g.* mixture of J- and H-like aggregates).

Table S15. Hopping parameter ($J_{m,n}$) and geometric parameters of dyes in Cy5 tBu-H heterodimers

Heterodimer Cy5 tBu-H	Position in HJ DNA	$J_{m,n}$ (meV)	$R_{m,n}$ (nm)	$dmin_{m,n}$ (nm)	Θ_{1s} (°)	Θ_{2s} (°)	Θ_t (°)	$\alpha_{m,n}$ (°)
Adjacent dimers	AB	98	0.47	0.34	90	79	9	14
	BA	92	0.52	0.34	88	79	4	14
	BC*	93	0.46	0.35	77	66	16	19
		46	1.47	0.35	30	51	6	81
	CB*	91	0.48	0.36	90	82	-1	9
		45	1.30	0.34	61	35	-2	84
	CD*	72	0.57	0.39	85	71	9	17
		45	1.44	0.34	23	49	-17	71
	DC*	76	0.52	0.38	56	62	1	6
		43	1.49	0.35	13	43	2	56
	AD	87	0.56	0.34	88	77	-1	16
	DA	91	0.48	0.34	87	82	5	12
Transverse dimers	AC	112	0.43	0.34	89	85	-3	7
	CA	92	0.47	0.34	80	89	-11	16
	BD	108	0.44	0.34	88	80	-5	9
	DB	106	0.42	0.34	84	90	-5	8

* Modeling results of dimer with subpopulations, the distance between dimers is ~1,000 nm

$J_{m,n}$ was calculated fitting the circular dichroism and absorption spectra and parameters calculated for monomers. Γ (eV) for dimers modeling was the average between the two participant dyes.

Table S16. Coordinates of dyes describing each dye orientation and position in Cy5 tBu-H heterodimers.

Heterodimer Cy5 tBu-H	Position in DNA-HJ	Dye 1					Dye 2				
		Θ_m (°)	Φ_m (°)	x_m (nm)	y_m (nm)	z_m (nm)	Θ_n (°)	Φ_n (°)	x_n (nm)	y_n (nm)	z_n (nm)
Adjacent dimers	AB	90	0	0.00	0.00	-0.24	101	9	0.00	0.00	0.24
	BA	92	0	0.00	0.00	-0.26	79	4	0.00	0.00	0.26
	BC*	103	0	0.00	0.00	-0.23	114	16	0.00	0.00	0.23
		30	0	0.00	0.00	-0.73	129	6	0.00	0.00	0.73
	CB*	90	0	0.00	0.00	-0.24	98	-1	0.00	0.00	0.24
		119	0	0.00	0.00	-0.65	35	-2	0.00	0.00	0.65
	CD*	95	0	0.00	0.00	-0.29	109	9	0.00	0.00	0.29
		157	0	0.00	0.00	-0.72	49	-17	0.00	0.00	0.72
	DC*	56	0	0.00	0.00	-0.26	62	1	0.00	0.00	0.26
		167	0	0.00	0.00	-0.75	43	2	0.00	0.00	0.75
	AD	92	0	0.00	0.00	-0.28	77	-1	0.00	0.00	0.28
	DA	93	0	0.00	0.00	-0.24	82	5	0.00	0.00	0.24
Transverse dimers	AC	91	0	0.00	0.00	-0.21	85	-3	0.00	0.00	0.21
	CA	80	0	0.00	0.00	-0.23	91	-11	0.00	0.00	0.23
	BD	92	0	0.00	0.00	-0.22	100	-5	0.00	0.00	0.22
	DB	96	0	0.00	0.00	-0.21	90	-5	0.00	0.00	0.21

Data depict the standard orientation and position of dimers.

* Modeling results of dimer with subpopulations, the distance between dimers is ~1,000 nm

Table S17. Goodness of fit and fit weight of Cy5 tBu-H heterodimers

Heterodimer Cy5 tBu-H	Position in DNA-HJ	Goodness of fit results						Goodness of fit weight						W_{absCD}rms
		rr	OI_{abs}	OI_{CD}	OI_{total}	MSD_{ABS}	MSD_{CD}	rr	OI_{abs}	OI_{CD}	OI_{total}	MSD_{ABS}	MSD_{CD}	
Adjacent dimers	AB	1.03	0.97	0.98	0.98	0.61	0.36	1	0	0	1	1	1	0.96
	BA	1.00	0.96	0.95	0.95	0.86	0.94	1	0	0	1	1	1	1.80
	BC	1.08	1.00	0.94	0.97	0.15	1.00	1	0	0	1	1	1	1.15
	CB	0.92	0.99	0.61	0.80	0.34	8.07	1	0	0	1	5	1	9.79
	CD	0.96	0.99	0.95	0.97	0.47	0.64	1	0	0	1	1	1	1.11
	DC	0.87	0.99	0.83	0.91	0.33	2.54	1	0	0	1	5	1	4.21
	AD	1.02	0.97	0.91	0.94	0.64	1.59	1	0	0	1	1	1	2.24
	DA	1.01	0.96	0.97	0.96	1.01	0.61	1	0	0	1	1	1	1.62
Transverse dimers	AC	1.00	0.96	0.97	0.96	0.89	0.62	1	0	0	1	1	1	1.51
	CA	1.02	0.98	0.98	0.98	0.52	0.33	1	0	0	1	1	1	0.85
	BD	1.01	0.97	0.98	0.97	0.72	0.47	1	0	0	1	1	1	1.18
	DB	1.00	0.96	0.98	0.97	0.79	0.57	1	0	0	1	1	1	1.36

SI-4.3.2. KRM results of Cy5 Peg-Cl

Table S18. Parameters of monomer Cy5-Peg and Cy5-Cl

Dye	Position in DNA-HJ	E_v (eV)	*D* (dimensionless)	Γ (eV)	E0 (eV)	M (Debye)	*L* (nm)
Cy5 Peg	A	0.142	0.935	0.049	1.84	14.2	1.4
	B	0.136	0.925	0.042	1.83	14.5	1.4
	C	0.139	0.950	0.045	1.84	14.2	1.4
	D	0.144	0.920	0.053	1.85	13.9	1.4
Cy5 Cl	A	0.132	0.795	0.040	1.86	13.4	1.4
	B	0.135	0.815	0.037	1.88	13.5	1.4
	C	0.136	0.815	0.039	1.88	13.7	1.4
	D	0.142	0.830	0.043	1.87	13.2	1.4

Table S19. Input fitting parameters used in calculation Cy5 Peg-Cl heterodimers

Heterodimer Cy5 H-Cl	Position in DNA HJ	#Chromophores	nv	E_{off} (meV)	Γ (eV)	c_{dis} (nm)
Adjacent dimers	AB	4	3	10	0.043	0.34
	BA	4	3	10	0.041	0.34
	BC	2	3	10	0.041	0.34
	CB	2	3	10	0.041	0.34
	CD	2	3	10	0.044	0.34
	DC	2	3	10	0.046	0.34
	AD	4	3	10	0.046	0.34
	DA	2	3	10	0.046	0.34
Transverse dimers	AC	2	3	10	0.044	0.34
	CA	2	3	10	0.043	0.34
	BD	2	3	10	0.043	0.34
	DB	2	3	10	0.045	0.34

*Four chromophores were used to fit only dimer with subpopulations (*e.g.* mixture of J- and H-like aggregates).

Table S20. Hopping parameter ($J_{m,n}$) and geometric parameters of dyes in Cy5 Peg-Cl heterodimers

Heterodimer Cy5 Peg-Cl	Position in HJ DNA	$J_{m,n}$ (meV)	$R_{m,n}$ (nm)	$dmin_{m,n}$ (nm)	Θ_{1s} (°)	Θ_{2s} (°)	Θ_t (°)	$\alpha_{m,n}$ (°)
Adjacent dimers	AB	86	0.52	0.35	66	56	11	14
		30	1.97	0.46	19	7	38	24
	BA	110	0.46	0.34	81	89	8	13
		10	1.66	0.94	89	29	0	63
	BC	50	1.31	0.35	30	60	7	90
	CB	54	1.20	0.34	66	42	1	72
	CD	50	1.34	0.34	33	58	3	88
	DC	53	1.24	0.34	42	63	-3	75
	AD	84	0.52	0.41	71	79	8	11
		42	1.51	0.84	87	28	56	78
	DA	52	1.23	0.34	41	65	1	75
Transverse dimers	AC	116	0.44	0.34	88	80	2	8
	CA	127	0.40	0.34	86	90	-1	4
	BD	100	0.51	0.34	86	81	-2	13
	DB	96	0.53	0.34	88	78	-2	14

* Modeling results of dimer with subpopulations, the distance between dimers is ~1,000 nm

$J_{m,n}$ was calculated fitting the circular dichroism and absorption spectra and parameters calculated for monomers. Γ (eV) for dimers modeling was the average between the two participant dyes.

Table S21. Coordinates of dyes describing each dye orientation and position in Cy5 Peg-Cl heterodimers.

Heterodimer Cy5 Peg-Cl	Position in DNA-HJ	Dye 1					Dye 2				
		Θ_m (°)	Φ_m (°)	x_m (nm)	y_m (nm)	z_m (nm)	Θ_n (°)	Φ_n (°)	x_n (nm)	y_n (nm)	z_n (nm)
Adjacent dimers	AB*	66	0	0.00	0.00	-0.26	56	11	0.00	0.00	0.26
		161	0	0.00	0.00	-0.99	7	38	0.00	0.00	0.99
	BA*	99	0	0.00	0.00	-0.23	89	8	0.00	0.00	0.23
		89	0	0.00	0.00	-0.83	151	0	0.00	0.00	0.83
	BC	30	0	0.00	0.00	-0.66	120	7	0.00	0.00	0.66
	CB	66	0	0.00	0.00	-0.60	138	1	0.00	0.00	0.60
	CD	147	0	0.00	0.00	-0.67	58	3	0.00	0.00	0.67
	DC	42	0	0.00	0.00	-0.62	117	-3	0.00	0.00	0.62
	AD*	109	0	0.00	0.00	-0.26	101	8	0.00	0.00	0.26
		87	0	0.00	0.00	-0.75	152	56	0.00	0.00	0.75
	DA	41	0	0.00	0.00	-0.61	115	1	0.00	0.00	0.61
Transverse dimers	AC	92	0	0.00	0.00	-0.22	100	2	0.00	0.00	0.22
	CA	86	0	0.00	0.00	-0.20	90	-1	0.00	0.00	0.20
	BD	86	0	0.00	0.00	-0.26	99	-2	0.00	0.00	0.26
	DB	88	0	0.00	0.00	-0.26	102	-2	0.00	0.00	0.26

Data depict the standard orientation and position of dimers.

* Modeling results of dimer with subpopulations, the distance between dimers is ~1,000 nm

Table S22. Goodness of fit and fit weight of Cy5 Peg-Cl heterodimers

Heterodimer Cy5 Peg-Cl	Position in DNA-HJ	Goodness of fit						Weight of fit						W_{absCD}rms
		rr	OI_{abs}	OI_{CD}	OI_{total}	MSD_{ABS}	MSD_{CD}	rr	OI_{abs}	OI_{CD}	OI_{total}	MSD_{ABS}	MSD_{CD}	
Adjacent dimers	AB	0.99	0.99	0.99	0.99	0.27	0.12	1.00	0	0	1	1	1	0.39
	BA	1.07	0.98	0.97	0.97	0.57	0.64	1.00	0	0	1	1	1	1.21
	BC	1.01	0.99	0.99	0.99	0.23	0.12	1.00	0	0	1	1	1	0.35
	CB	0.96	0.99	0.29	0.64	0.39	10.88	1.00	0	0	1	1	1	11.27
	CD	1.00	0.99	0.97	0.98	0.13	0.51	1.00	0	0	1	1	1	0.64
	DC	1.02	1.00	0.90	0.95	0.15	1.49	1.00	0	0	1	1	1	1.64
	AD	0.97	1.00	0.83	0.91	0.12	3.02	1.00	0	0	1	1	1	3.13
	DA	0.95	0.99	0.59	0.79	0.29	8.45	1.00	0	0	1	1	1	8.74
Transverse dimers	AC	1.00	0.98	0.78	0.88	0.34	4.27	1.00	0	0	1	1	0	0.34
	CA	1.00	0.97	0.24	0.60	0.58	14.23	1.00	0	0	1	1	0	0.58
	BD	0.99	0.97	0.88	0.92	0.63	2.32	1.00	0	0	1	1	0	0.63
	DB	1.02	0.98	0.85	0.92	0.34	2.74	1.00	0	0	1	1	0	0.34

SI-4.3.3. KRM results of Cy5 H-Cl

Table S23. Parameters of monomer Cy5-H and Cy5-Cl

Dye	Position in DNA-HJ	E_v (eV)	*D* (dimensionless)	Γ (eV)	E0 (eV)	M (Debye)	*l* (nm)
Cy5-H	A	0.137	0.820	0.040	1.90	12.8	1.4
	B	0.133	0.810	0.037	1.90	12.9	1.4
	C	0.135	0.800	0.039	1.91	13.1	1.4
	D	0.140	0.820	0.043	1.90	13.0	1.4
Cy5-Cl	A	0.132	0.795	0.040	1.86	13.4	1.4
	B	0.135	0.815	0.037	1.88	13.5	1.4
	C	0.136	0.815	0.039	1.88	13.7	1.4
	D	0.142	0.830	0.043	1.87	13.2	1.4

Table S24. Input fitting parameters used in the calculation Cy5 H-Cl heterodimers

Heterodimer Cy5 H-Cl	Position in DNA-HJ	# Dyes	nv	E_{off} (meV)	Γ (eV)	c_{dis} (nm)
Adjacent dimers	AB	2	3	10	0.039	0.34
	BA	4	3	10	0.039	0.34
	BC	2	3	10	0.038	0.34
	CB	2	3	10	0.038	0.34
	CD	2	3	10	0.041	0.34
	DC	2	3	10	0.041	0.34
	AD	4	3	10	0.042	0.34
	DA	2	3	10	0.042	0.34
Transverse dimers	AC	2	3	15	0.040	0.34
	CA	2	3	15	0.040	0.34
	BD	2	3	15	0.040	0.34
	DB	2	3	15	0.040	0.34

*Four chromophores were used to fit only dimer with subpopulations (*e.g.* mixture of J- and H-like aggregates).

Table S25. Hopping parameter ($J_{m,n}$) and geometric parameters of dyes in Cy5 H-Cl heterodimers

Heterodimer Cy5 H-Cl	Position in DNA-HJ	$J_{m,n}$ (meV)	$R_{m,n}$ (nm)	$dmin_{m,n}$ (nm)	Θ_{1s} (°)	Θ_{2s} (°)	Θ_t (°)	$\alpha_{m,n}$ (°)
Adjacent dimers	AB	48	1.25	0.34	39	64	1	77
	BA*	89	0.51	0.34	90	76	8	16
		30	1.62	0.47	50	27	2	77
	BC	47	1.34	0.34	58	37	1	85
	CB	48	1.30	0.34	36	61	3	84
	CD	47	1.31	0.34	60	37	-2	83
	DC	48	1.31	0.34	60	37	1	83
	AD*	72	0.62	0.36	78	83	5	19
		43	1.42	0.35	52	22	2	73
	DA	41	1.35	0.38	56	49	-2	75
Transverse dimers	AC	91	0.52	0.34	79	88	-4	14
	CA	89	0.53	0.34	76	89	-5	16
	BD	85	0.54	0.34	89	76	-6	17
	DB	84	0.57	0.34	87	75	-9	20

* Modeling results of dimer with subpopulations, the distance between dimers is ~1,000 nm

$J_{m,n}$ was calculated fitting the circular dichroism and absorption spectra and parameters calculated for monomers. Γ (eV) for dimers modeling was the average between the two participant dyes.

Table S26. Coordinates of dyes describing each dye orientation and position in Cy5 H-Cl heterodimers.

Heterodimer Cy5 H-Cl	Position in DNA-HJ	Dye 1					Dye 2				
		Θ_m (°)	Φ_m (°)	x_m (nm)	y_m (nm)	z_m (nm)	Θ_n (°)	Φ_n (°)	x_n (nm)	y_n (nm)	z_n (nm)
Adjacent dimers	AB	141	0	0.00	0.00	-0.62	64	1	0.00	0.00	0.62
	BA*	90	0	0.00	0.00	-0.26	76	8	0.00	0.00	0.26
		130	0	0.00	0.00	-0.81	27	2	0.00	0.00	0.81
	BC	122	0	0.00	0.00	-0.67	37	1	0.00	0.00	0.67
	CB	144	0	0.00	0.00	-0.65	61	3	0.00	0.00	0.65
	CD	60	0	0.00	0.00	-0.66	143	-2	0.00	0.00	0.66
	DC	120	0	0.00	0.00	-0.66	37	1	0.00	0.00	0.66
	AD*	102	0	0.00	0.00	-0.31	83	5	0.00	0.00	0.31
		128	0	0.00	0.00	-0.71	22	2	0.00	0.00	0.71
	DA	124	0	0.00	0.00	-0.67	49	-2	0.00	0.00	0.67
Transverse dimers	AC	79	0	0.00	0.00	-0.26	92	-4	0.00	0.00	0.26
	CA	104	0	0.00	0.00	-0.27	89	-5	0.00	0.00	0.27
	BD	91	0	0.00	0.00	-0.27	76	-6	0.00	0.00	0.27
	DB	93	0	0.00	0.00	-0.28	75	-9	0.00	0.00	0.28

Data depict standard orientation and position of dimers.

* Modeling results of the dimers with subpopulations, the distance between dimers is ~1,000 nm

Table S27. Goodness of fit and fit weight of Cy5 H-Cl heterodimers

Heterodimer Cy5 Peg-Cl	Position in DNA-HJ	Goodness of fit						Weight of fit						W_{absCD}rms
		rr	OI_{abs}	OI_{CD}	OI_{total}	MSD_{ABS}	MSD_{CD}	rr	OI_{abs}	OI_{CD}	OI_{total}	MSD_{ABS}	MSD_{CD}	
Adjacent dimers	AB	0.95	0.99	0.88	0.93	0.32	1.77	1.00	0	0	1	1	0	0.32
	BA	0.97	0.99	0.98	0.98	0.66	0.43	1.00	0	0	1	1	1	1.09
	BC	1.00	0.99	0.67	0.83	0.21	3.59	1.00	0	0	1	1	1	3.80
	CB	0.95	0.99	0.87	0.93	0.33	1.67	1.00	0	0	1	1	0	0.33
	CD	0.98	0.99	0.92	0.96	0.18	1.07	1.00	0	0	1	1	1	1.25
	DC	1.00	0.99	0.53	0.76	0.19	7.51	1.00	0	0	1	1	0	0.19
	AD	0.99	0.99	0.97	0.98	0.24	0.64	1.00	0	0	1	1	1	0.88
	DA	1.01	0.99	0.96	0.97	0.33	0.59	1.00	0	0	1	1	1	0.93
Transverse dimers	AC	1.03	0.97	0.96	0.96	0.80	0.70	1.00	0	0	1	1	1	1.50
	CA	1.00	0.96	0.98	0.97	0.80	0.51	1.00	0	0	1	1	1	1.31
	BD	0.99	0.97	0.97	0.97	0.64	0.79	1.00	0	0	1	1	1	1.43
	DB	1.04	0.97	0.97	0.97	0.65	0.44	1.00	0	0	1	1	1	1.09

SI-5. Conformers of DNA-HJ and impact on dye interaction

Unlabeled DNA-HJ (without dyes) can adopt different conformers depending on the salt concentration in the solution. The predominant conformers at higher than ~5mM Mg^{2+} are the isomeric forms, *Iso I* and *Iso II*, [9–11] characterized by their co-axially stacked arms on each other.[9] In the present study, the dye-DNA-HJ constructs were synthesized in 15 mM $MgCl_2$, a condition to have *Iso I* and *Iso II* conformers (Figure S5-1). The two points of attachment of Cy5-R in the adjacent or transverse position of the center branch of *Iso* DNA-HJ structures could impact the dye interaction by making the DNA backbone more rigid. Hence, based on the potential DNA conformer, the expected optical properties was listed in Figure S5-2.

On the other hand, the position of dyes along the DNA-HJ impacts the arrangements of the dye in the aggregates. Adjacent positions of dyes in the *Iso* DNA-HJ conformer seem to promote a π-teeing stacking of dyes (perpendicular T-shape) (Figure S5-1B). This type of stacking can exhibit a great center-to-center dye distance ($R_{m,n}$) and angle between the transition dipole moments (TDM) of dyes ($\alpha_{m,n}$) that reduces the dye-dye interaction that results in a small exciton hopping parameter ($J_{m,n}$). Additionally, π-teeing stacking may lead to a fluctuation in the dye-dye interaction due to the limited area of dyes to interact with each other, resulting in dimer with subpopulations that exhibit different $J_{m,n}$. In contrast, transverse positions of dyes in the *Iso* DNA-HJ conformer seem to promote a π-stacking (face-to-face or sandwich shape) of dyes with small $R_{m,n}$ and $\alpha_{m,n}$ (Figure S5-1C), resulting in a strong dye-dye interaction with a large $J_{m,n}$. This interpretation given for adjacent and transverse dimers based on the DNA-HJ conformers agrees with the result obtained using KRM modeling, which indicates that adjacent dimers have smaller $J_{m,n}$ compared to transverse dimers. Besides, some adjacent dimers samples form dimers with subpopulations that have different $J_{m,n}$ values (Section 3.3 of the main text and Section S4).

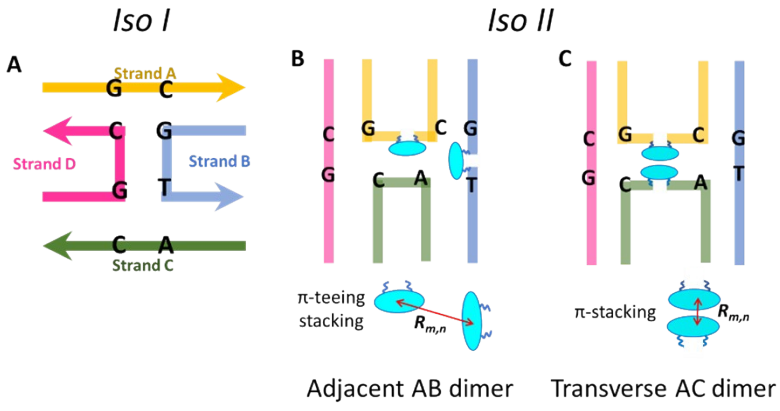

Figure S35. Schematic representation of major conformations of DNA-HJ (*Iso I* and *Iso II*) depicting the position of dyes and nucleobase pairs in the central point of each arm. [A] unlabeled (without dye) DNA-HJ. [B] adjacent dimer in a potentially predominant Iso II conformer of DNA-HJ that led to dye packing with a large angle between the TDM of dyes and long center-to-center dye distance. [C] transverse dimer in a potentially predominant Iso II conformer of DNA-HJ that led to dye packing with a small angle between the TDM of dyes and short center-to-center dye distance.

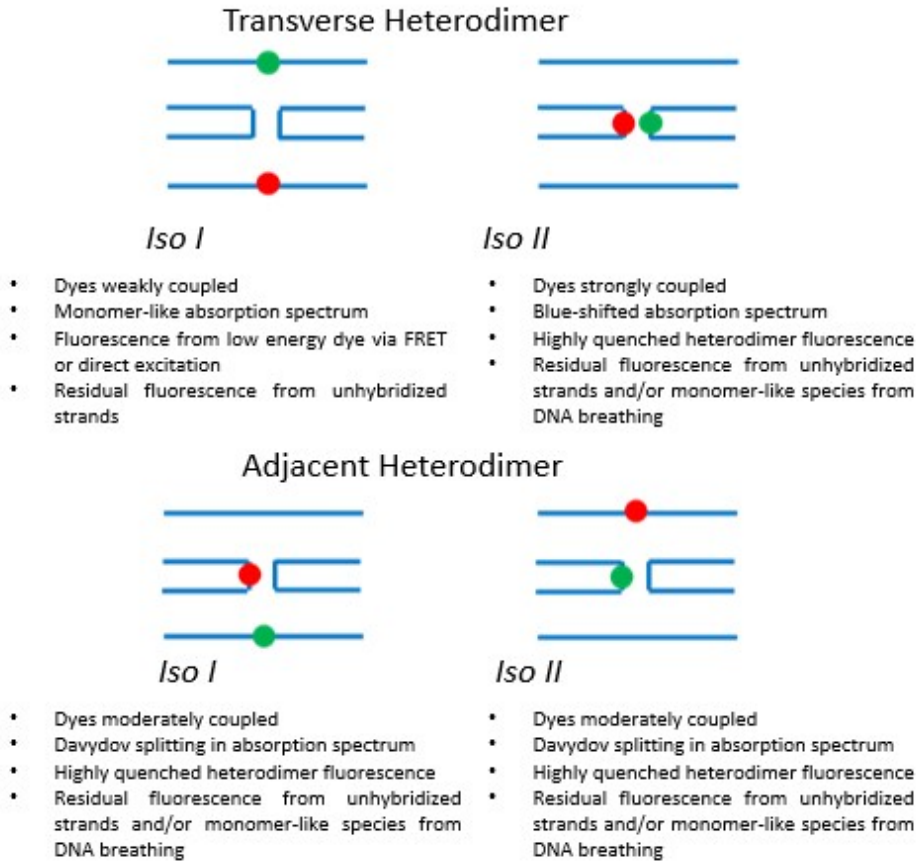

Figure S36. Closed form structural isomers, *Iso I* and *Iso II*, for the DNA-HJ showing the relative positioning of dye heterodimers, and the expected optical properties listed for each isomer. Top: Transverse heterodimers. Bottom: Adjacent heterodimers.

SI-6. Relationship between dye properties and $J_{m,n}$

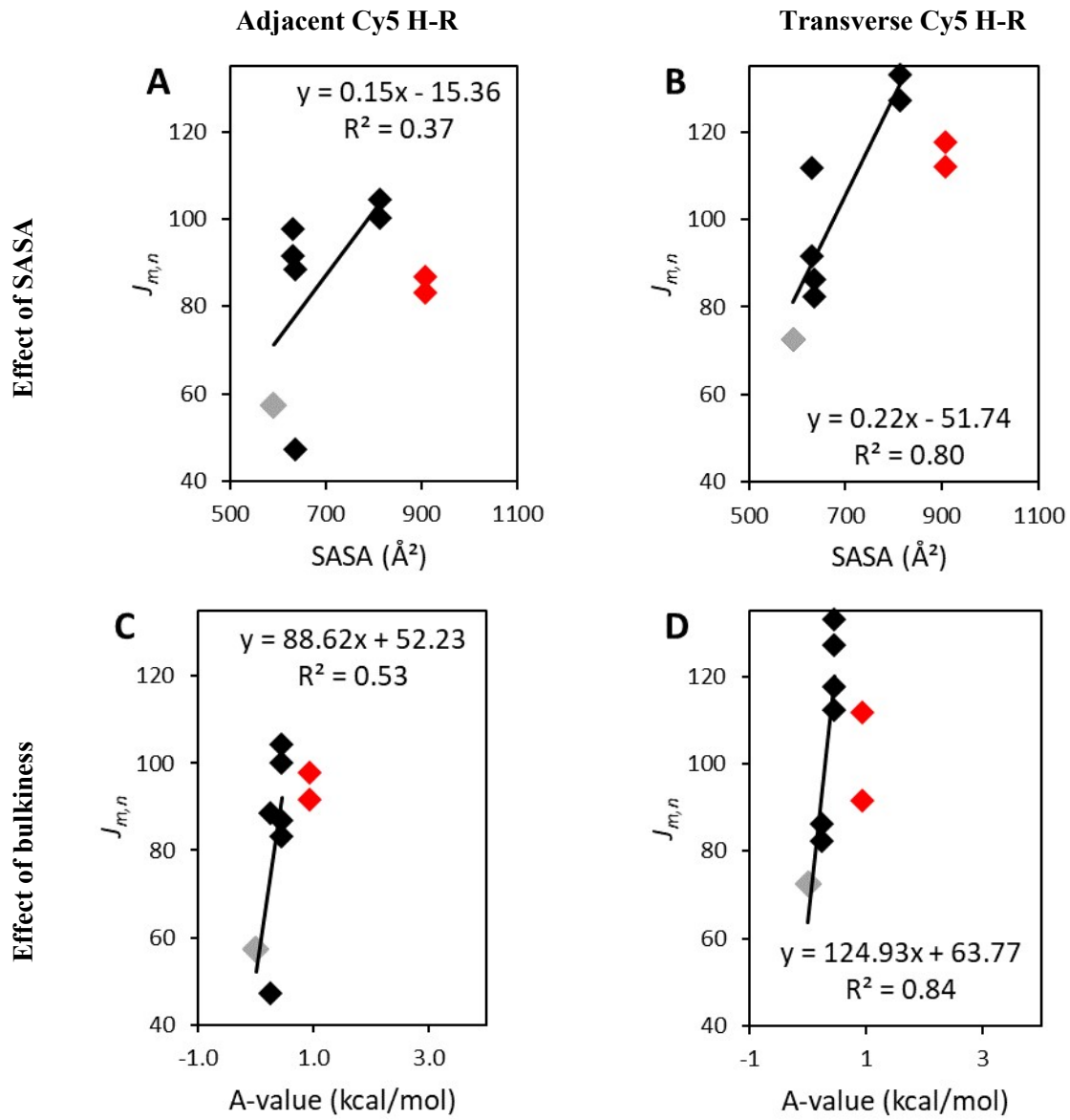

Figure S37. Relationship between $J_{m,n}$ and Cy5 H-R properties, SASA [A and B] and A-value [C and D]. Outliers (red diamond) of SASA and A-value analysis are Cy5 H-Peg and Cy5 H-tBu heterodimers, respectively. The grey diamond represents $J_{m,n}$ of homodimers relative to the respective SASA and A-value. The equation of linear regression analysis excludes outliers.

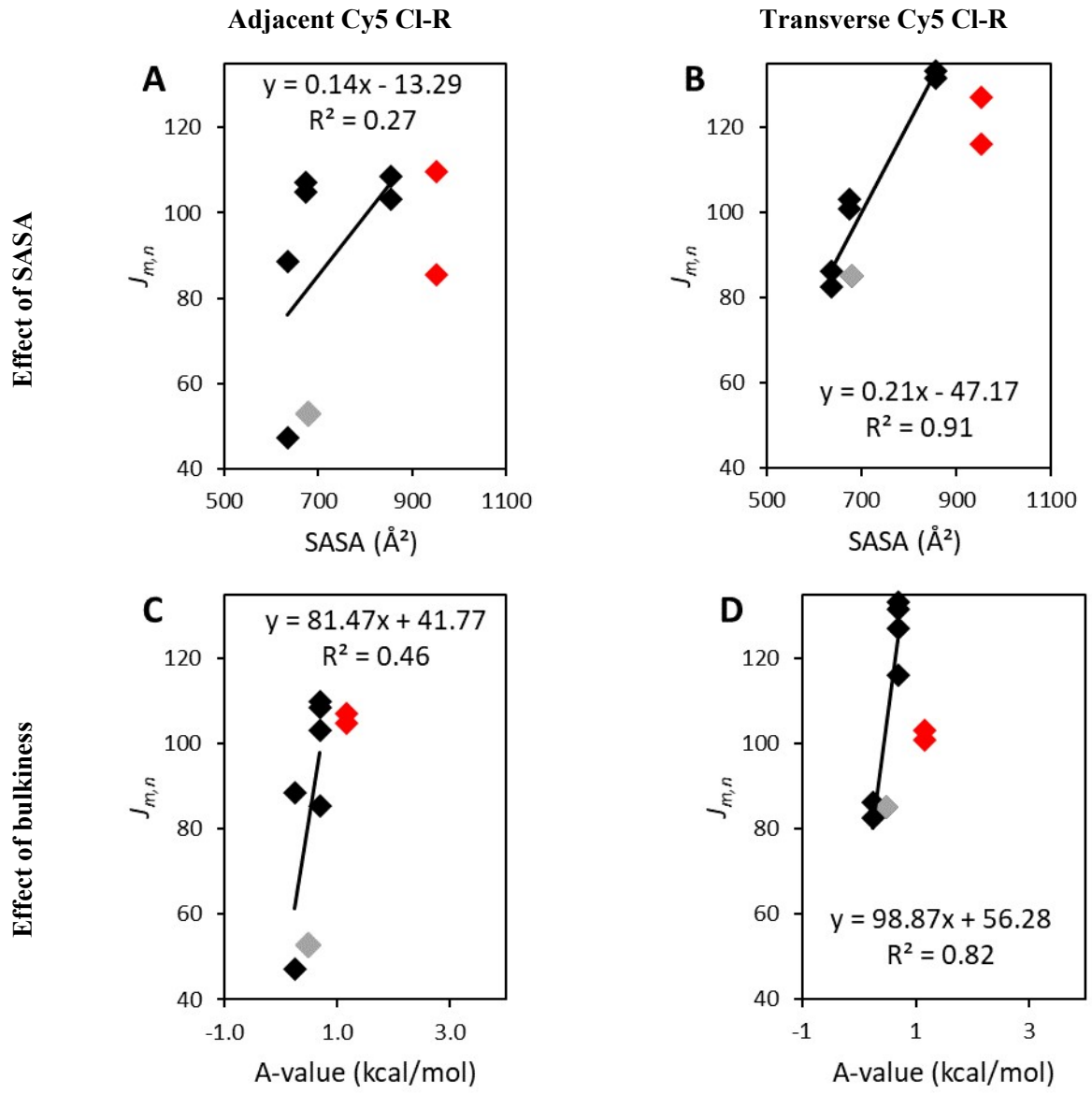

Figure S38. Relationship between $J_{m,n}$ and Cy5 Cl-R properties, SASA [A and B] and A-value [C and D]. Outliers (red diamond) of SASA and A-value analysis are Cy5 Cl-Peg and Cy5 Cl-tBu heterodimers, respectively. The grey diamond represents $J_{m,n}$ of homodimers relative to the respective SASA and A-value. The equation of linear regression analysis excludes outliers.

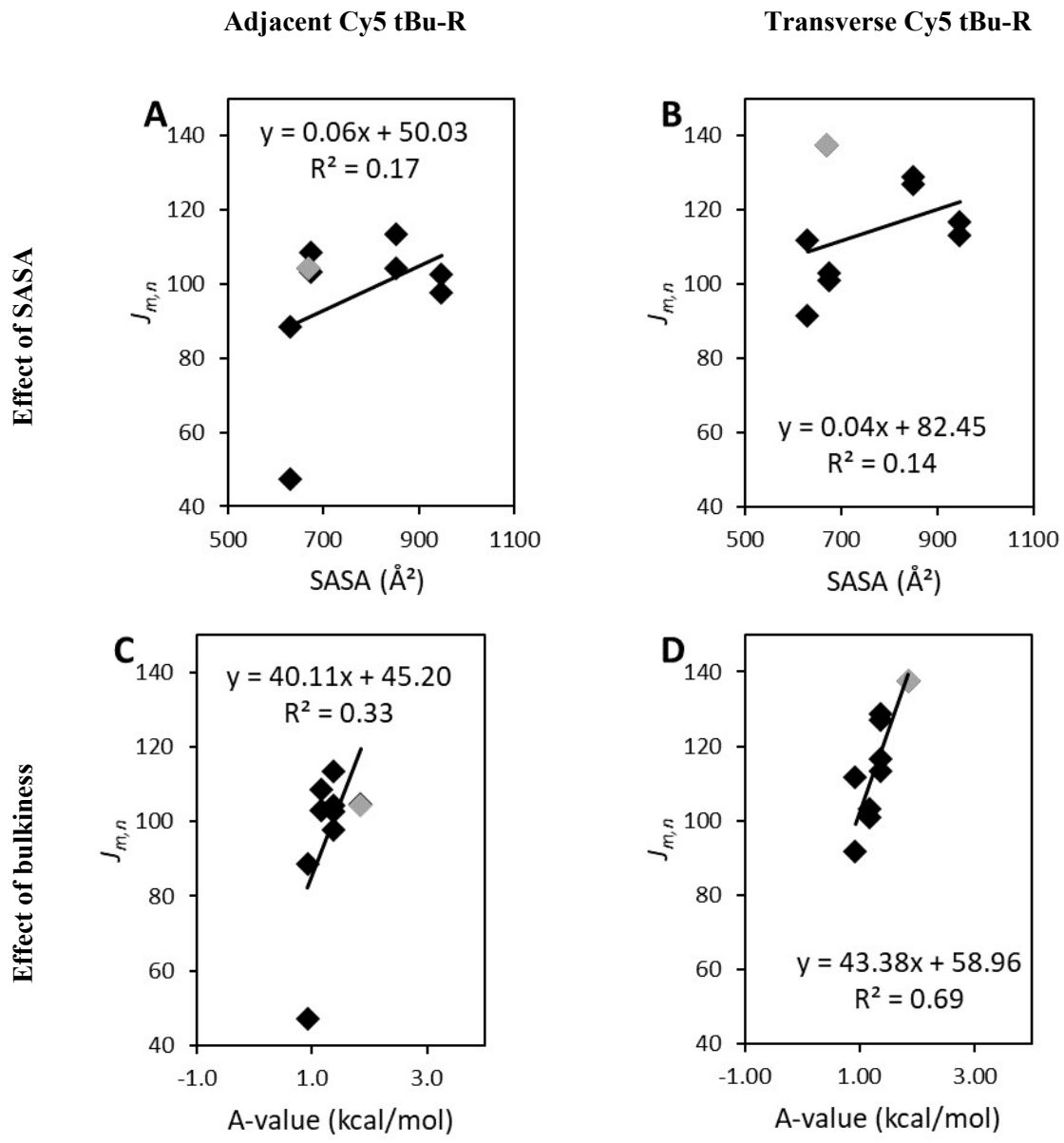

Figure S39. Relationship between $J_{m,n}$ and Cy5tBu-R properties SASA [A and B] and A-value [C and D]. The grey diamond represents $J_{m,n}$ of homodimers relative to the respective SASA and A-value

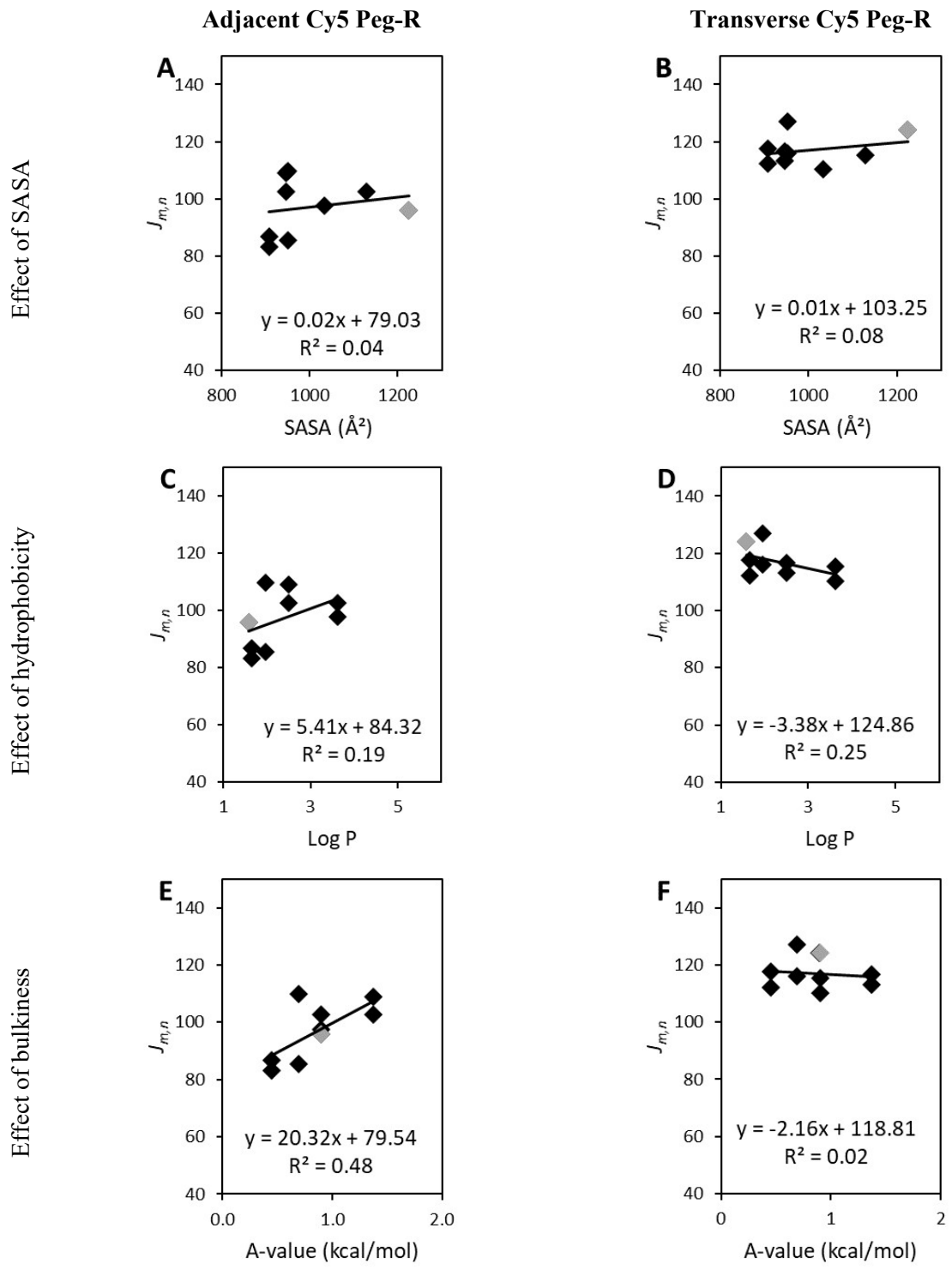

Figure S40. Relationship between $J_{m,n}$ and Cy5 Peg-R properties, SASA [A and B], Log P [C and D], and A-value [E and F]. The grey diamond represents $J_{m,n}$ of homodimers relative to the respective SASA, log P, and A-value.

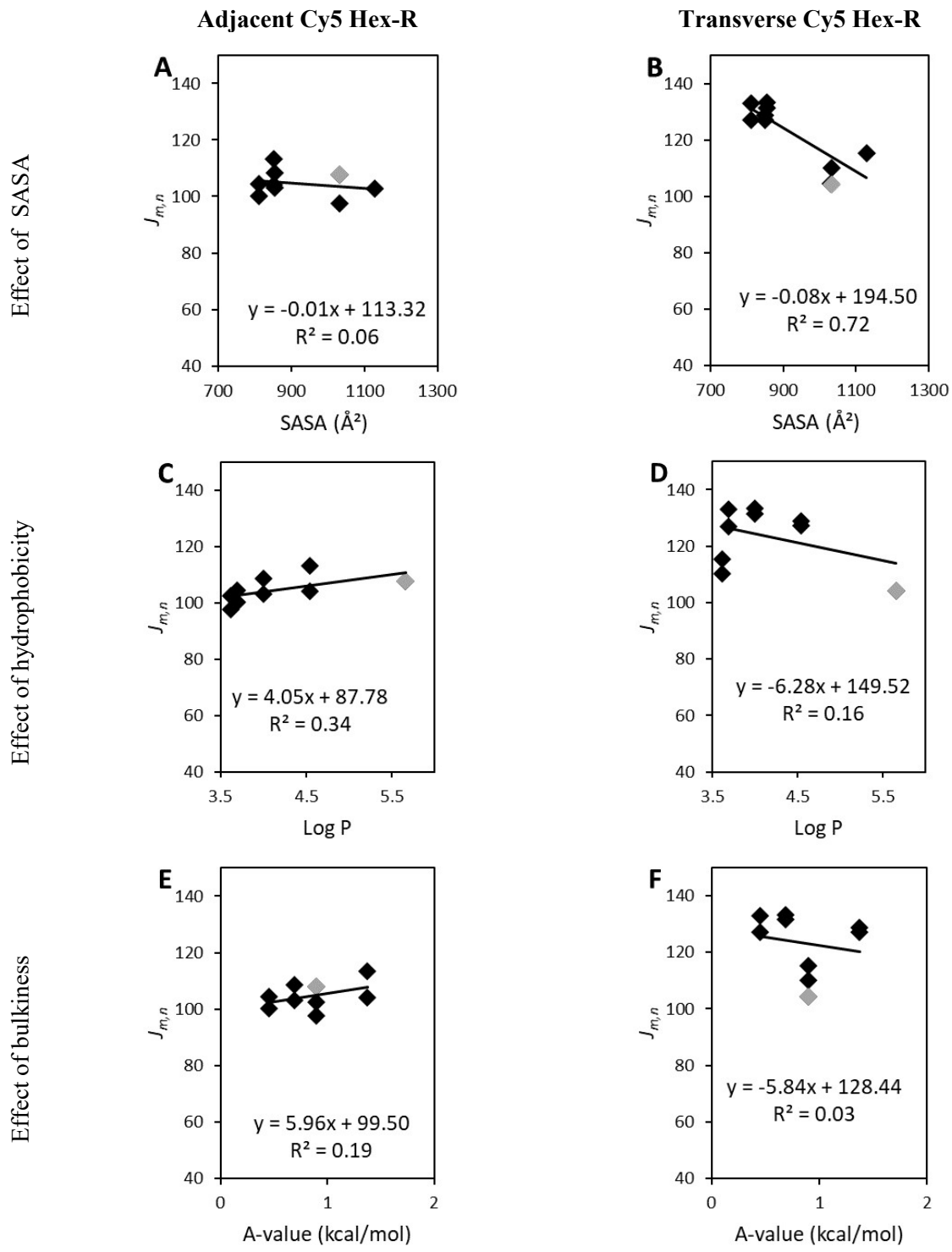

Figure S41. Relationship between $J_{m,n}$ and Cy5 Hex-R properties SASA [A and B], Log P [C and D], and A-value [E and F]. The grey diamond represents $J_{m,n}$ of homodimers relative to the respective SASA, log P and A-value.

SI-7. TA signal decay kinetics for select monomers and dimers

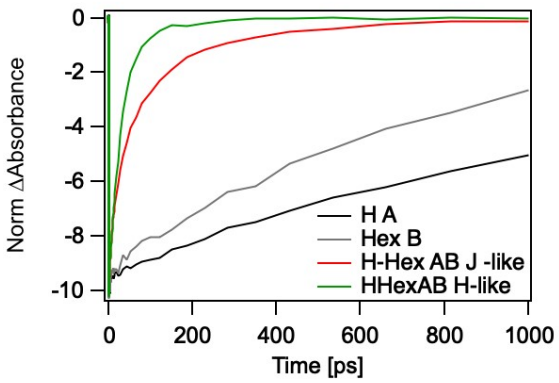

Figure S42. Signal decay kinetics of Cy5-H A monomer, Cy5-hex B monomer, Cy5-H/Cy5-hex AB dimers photoselected at different pumping wavelengths (682 nm for Cy5-hex monomer and J-like dimer; 653 nm for Cy5-H A monomer and H-like dimer).

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