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Photon Harvesting by Excimer-Forming Multichromophores

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Electronic Supplementary information

(ESI)

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Table of Contents

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Synthetic and analytical procedure

Oligonucleotide-synthesis was performed by an automated oligonucleotide synthesis on a 394-DNA/RNA synthesizer (*Applied Biosystems*), based on phosphoramidite chemistry. The building blocks carboxamide pyrene (X)[1] was synthesized as previously described. The Cy5 phosphoramidite was obtained from Glen Research, 22825 Davis Drive, Sterling, Virginia, 20164. The unmodified strand was obtained commercially from Microsynth, Balgach, Switzerland. Modified oligonucleotides with a pyrene unit at the 3'-end were synthesized on a pyrene modified CPG solid support (controlled pore glass). Cleavage from the solid support and final deprotection was done by treatment with 30% NH_4OH solution at 55°C overnight. Oligomeres containing Cy5 phosphormaidite were cleaved form the solid support and deprotected for 12 h at room temperature with 30% NH_4OH solution.

Reverse-phase HPLC purification of oligonucleotides were done using a reversed HPLC (Shimadzu SCL-10A VP with a diode array detector, column: Lichrospher 100 RP-18, 5µm, 240 x 4 mm, Dr. Maisch GmbH); eluent A = acetic acid : triethylamin (1:1) 0.1 M (pH 7.4), eluent B = acetonitrile; gradient 5-50% over 30 min. Some oligonucleotides were purified with a smaller gradient (5-30%) over 40 min to increase oligonucleotide separation.

Molecular mass determinations of oligonucleotides were performed with a SciexQTrap (hybrid triple quadrupole/linear ion trap, *Applied Biosystems*) equipped with a TurbolonSpray® source, ESI-MS (negative mode, CH_3CH/H_20 + 1% TEA).

Oligonucleotide concentrations were determined using oligonucleotide solutions, which were diluted to 1% and the absorbance of Cy5 at 646 nm was measured on a Varian Cary 100 Bio UV-Visible spectrophotometer equipped with a Varian Cary temperature controller. The epsilon of Cy5 was taken to be 250'000 $M^{-1}cm^{-1}$ at 90°C, in order to calculate the oligonucleotide concentrations containing Cy5. The concentration of the complementary strand without Cy5 was determined by monitoring the pyrene absorption at 350 nm, so that the pyrene absorption was equal to the pyrene absorption of the oligonucleotide containing Cy5. The concentration of the reference material containing no pyrene was determined by comparing the absorption at 260 nm using epsilon values 15300 $M^{-1}cm^{-1}$, 11700 $M^{-1}cm^{-1}$, 7400 $M^{-1}cm^{-1}$ and 9000 $M^{-1}cm^{-1}$ for A, G, C and T, respectively.
Samples with adjusted pyrene absorbance were prepared by manually diluting the systems. Therefore, the concentrations of the oligomers are different in each sample. E.g. for sample with hybrid **3*4** the single strand concentration is approximately 0.5 µM, whereas the sample with hybrid **9*10** was diluted to obtain the same pyrene absorbance.

Thermal denaturation experiments were performed with 1.0 µM single strand oligonucleotide concentration in 100 mM NaCl and 10 mM phosphate buffer (pH 7.4) on Varian Cary 100 Bio UV-Visible spectrophotometer equipped with a Varian Cary temperature controller. The data were

collected at various wavelengths such as 245, 260, 270 and 350 nm (cooling-heating-cooling cycles in the temperature range of 10°C - 90°C, temperature gradient of 0.5°C/min, data points recorded every 0.5°C). Temperature melting values (T_m) were determined as the maximum of the first derivative of the melting curves.

Temperature-dependent UV-Vis spectra were acquired form 90°C to 20°C on a Varian Cary 100 Bio UV-Visible spectrophotometer equipped with a Varian Cary temperature controller. All experiments were carried out at a 1.0 µM single strand oligonucleotide concentration in 100 mM NaCl and 10 mM phosphate buffer (pH 7.4).

Temperature-dependent fluorescence spectra were acquired from 90°C to 20°C on a Varian Cary Eclipse fluorescence spectrophotometer equipped with a Varian Cary temperature controller. For emission spectra the excitation wavelength was set at 350 nm and for excitation spectra the emission wavelength was set at 670 nm. In all experiments the photo multiplier tube (PMT) voltage was set to 600 V.

Investigated oligonucleotide sequences and masses

Table S1 Overview of the investigated oligomer sequences with the molecular formula, calculated and found average masses.

	Sequence	*molecular formula*	*calcd. avg. mass*	*found avg. mass*
1	5′GAG CAT TA	$C_{79}H_{99}N_{32}O_{45}P_7$	2433.6	2434.0
2	3′CTC GTA AT-**Cy5**	$C_{109}H_{138}N_{29}O_{51}P_8^+$	2918.2	2917.6
3	5′GAG CAT TA**S S**	$C_{127}H_{145}N_{36}O_{57}P_9$	3366.5	3367.1
4	3′CTC GTA AT**S S**-**Cy5**	$C_{157}H_{184}N_{33}O_{63}P_{10}^+$	3851.1	3850.8
5	5′GAG CAT TA**S SSS S**	$C_{199}H_{214}N_{42}O_{75}P_{12}$	4765.7	4766.4
6	3′CTC GTA AT**S SSS S**-**Cy5**	$C_{229}H_{253}N_{39}O_{81}P_{13}^+$	5250.3	5250.2
7	5′GAG CAT TA**S SSS SSS**	$C_{247}H_{260}N_{46}O_{87}P_{14}$	5698.6	5699.9
8	3′CTC GTA AT**S SSS SSS**-**Cy5**	$C_{277}H_{299}N_{43}O_{93}P_{15}^+$	6183.2	6183.0
9	5′GAG CAT TA**S SSS SSS SS**	$C_{295}H_{306}N_{50}O_{99}P_{16}$	6631.4	6632.39
10	3′CTC GTA AT**S SSS SSS SS**-**Cy5**	$C_{325}H_{345}N_{47}O_{105}P_{17}^+$	7116.0	7116.10

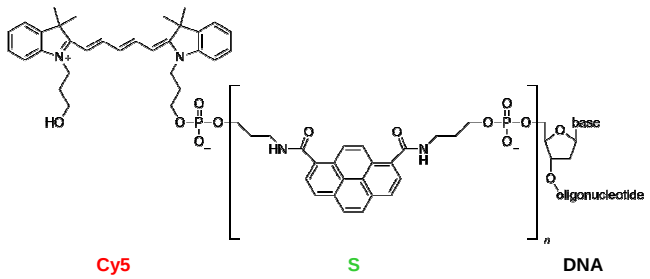


Fig. S1 Molecular structure of the investigated modified oligonucleotide.

[1] H. Bittermann, D. Siegemund, V. L. Malinovskii, R. Häner, *J.Am.Chem.Soc.*, 2008, **130**, 15285-15287.
[2] N. Rahe, C. Rinn, T. Carell, *Chem.Commun.*, 2003, 2119-2121.
[3] S. M. Biner, D. Kummer, V. L. Malinovskii, R. Häner, *Org.Biomol.Chem.*, 2011, **9**, 2628-2633.

HPLC chromatograms and ESI-MS data

Oligomer **2**

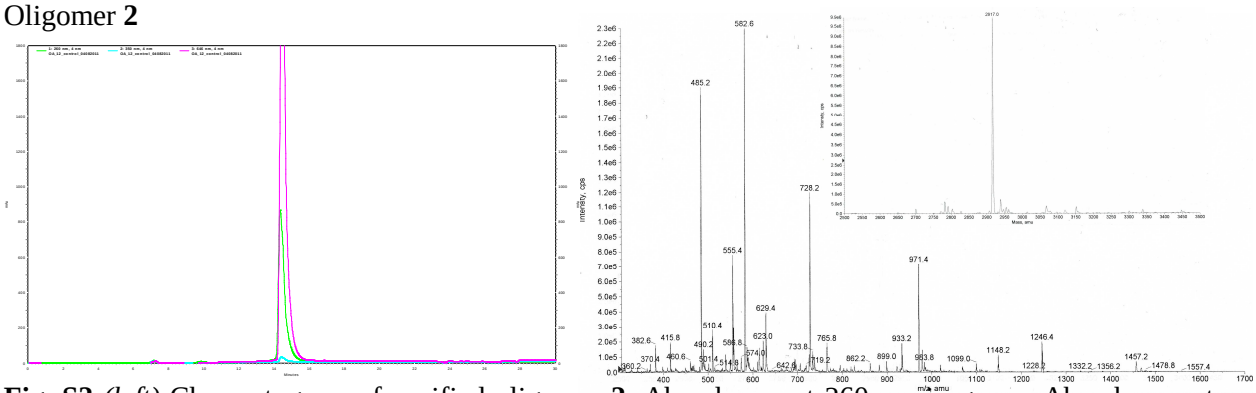


Fig. S2 *(left)* Chromatogram of purified oligomer **2**. Absorbance at 260 nm in green; Absorbance at 350 nm in blue; Absorbance at 646 nm in violet; Eluent A = $(Et_3NH)OAc$ (0.1 M, pH 7.4), Eluent B = MeCN; gradient 5 - 50 % B; t_R = 14.4 min. *(right)* ESI-MS of **2** with mass reconstruction; negative ion mode, acetonitrile/H_2O (1:1) + 1 % triethylammonium.

Oligomer **3**

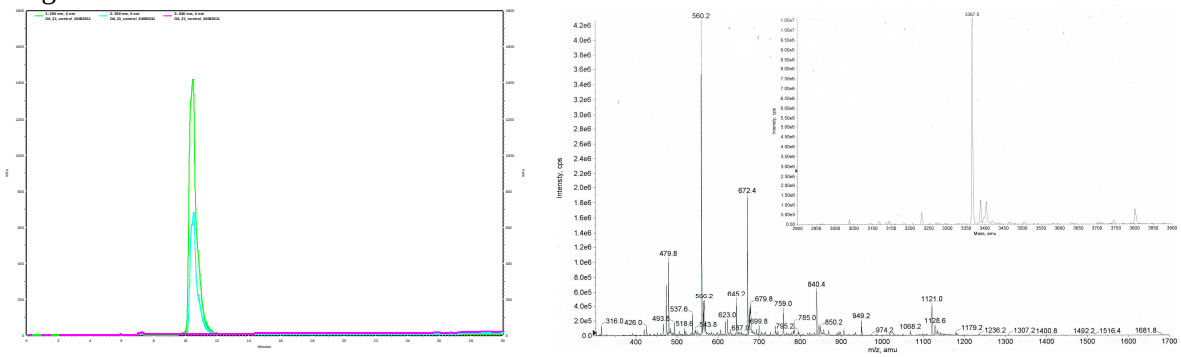


Fig. S3 *(top)* Chromatogram of purified oligomer **3**. Absorbance at 260 nm in green; Absorbance at 350 nm in blue; Absorbance at 646 nm in violet; Eluent A = $(Et_3NH)OAc$ (0.1 M, pH 7.4), Eluent B = MeCN; gradient 5 - 50 % B; t_R = 10.4 min. *(bottom)* ESI-MS of **3** with mass reconstruction; negative ion mode, acetonitrile/H_2O (1:1) + 1 % triethylammonium.

Oligomer **4**

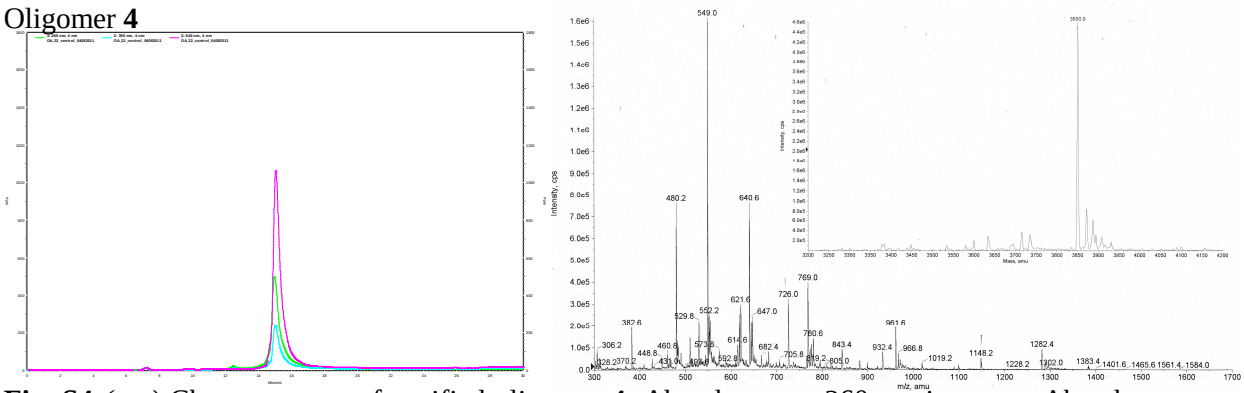


Fig. S4 *(top)* Chromatogram of purified oligomer **4**. Absorbance at 260 nm in green; Absorbance at 350 nm in blue; Absorbance at 646 nm in violet; Eluent A = $(Et_3NH)OAc$ (0.1 M, pH 7.4), Eluent B = MeCN; gradient 5 – 50 % B; t_R = 15.0 min. *(bottom)* ESI-MS of **4** with mass reconstruction; negative ion mode, acetonitrile/H_2O (1:1) + 1 % triethylammonium.

Oligomer **5**

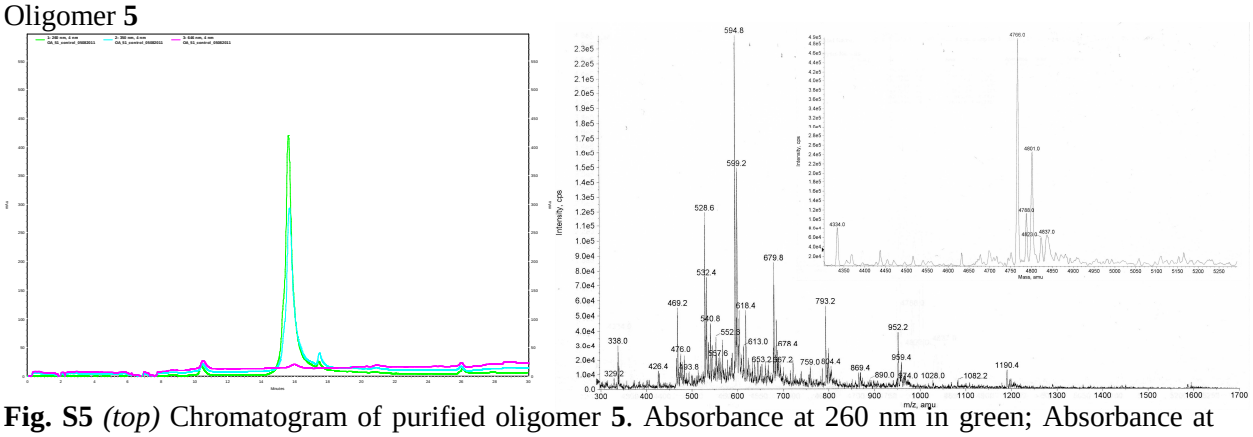


Fig. S5 *(top)* Chromatogram of purified oligomer **5**. Absorbance at 260 nm in green; Absorbance at 350 nm in blue; Absorbance at 646 nm in violet; Eluent A = (Et_3NH)OAc (0.1 M, pH 7.4), Eluent B = MeCN; gradient 5 – 50 % B; t_R = 15.7 min. *(bottom)* ESI-MS of **5** with mass reconstruction; negative ion mode, acetonitrile/H_2O (1:1) + 1 % triethylammonium.

Oligomer **6**

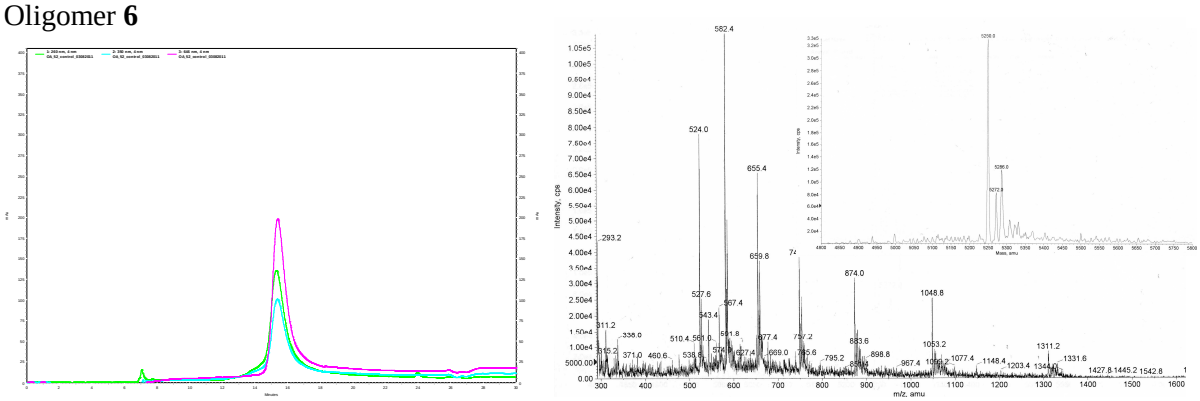


Fig. S6 *(top)* Chromatogram of purified oligomer **6**. Absorbance at 260 nm in green; Absorbance at 350 nm in blue; Absorbance at 646 nm in violet; Eluent A = (Et_3NH)OAc (0.1 M, pH 7.4), Eluent B = MeCN; gradient 5 – 50 % B; t_R = 15.3 min. *(bottom)* ESI-MS of **6** with mass reconstruction; negative ion mode, acetonitrile/H_2O (1:1) + 1 % triethylammonium.

Oligomer **7**

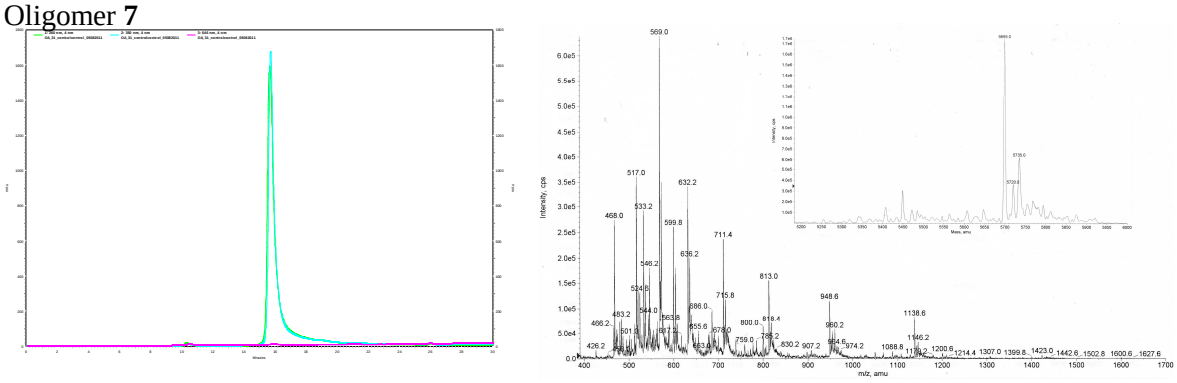


Fig. S7 *(top)* Chromatogram of purified oligomer **7**. Absorbance at 260 nm in green; Absorbance at 350 nm in blue; Absorbance at 646 nm in violet; Eluent A = (Et_3NH)OAc (0.1 M, pH 7.4), Eluent B = MeCN; gradient 5 – 50 % B; t_R = 15.7 min. *(bottom)* ESI-MS of **7** with mass reconstruction; negative ion mode, acetonitrile/H_2O (1:1) + 1 % triethylammonium.

Oligomer **8**

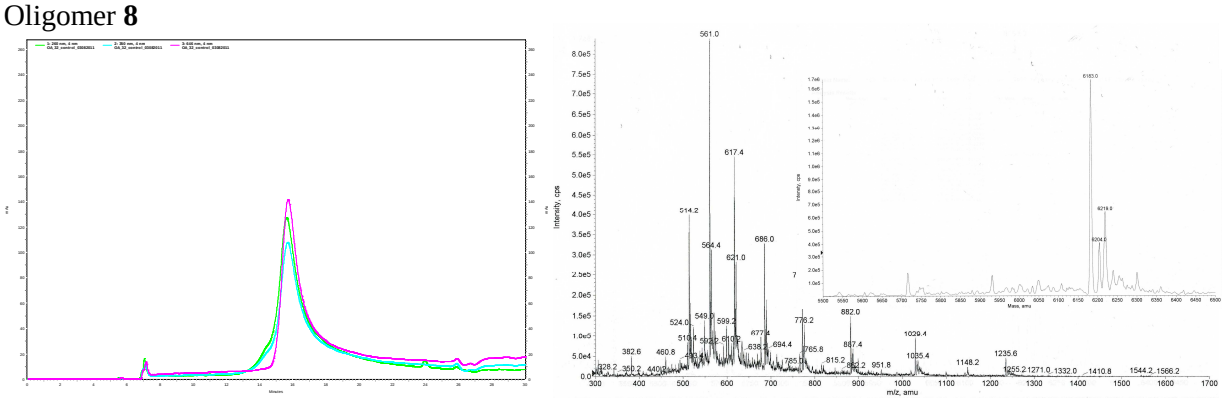


Fig. S8 *(top)* Chromatogram of purified oligomer **8**. Absorbance at 260 nm in green; Absorbance at 350 nm in blue; Absorbance at 646 nm in violet; Eluent A = $(Et_3NH)OAc$ (0.1 M, pH 7.4), Eluent B = MeCN; gradient 5 – 50 % B; t_R = 15.7 min. *(bottom)* ESI-MS of **8** with mass reconstruction; negative ion mode, acetonitrile/H_2O (1:1) + 1 % triethylammonium.

Oligomer **9**

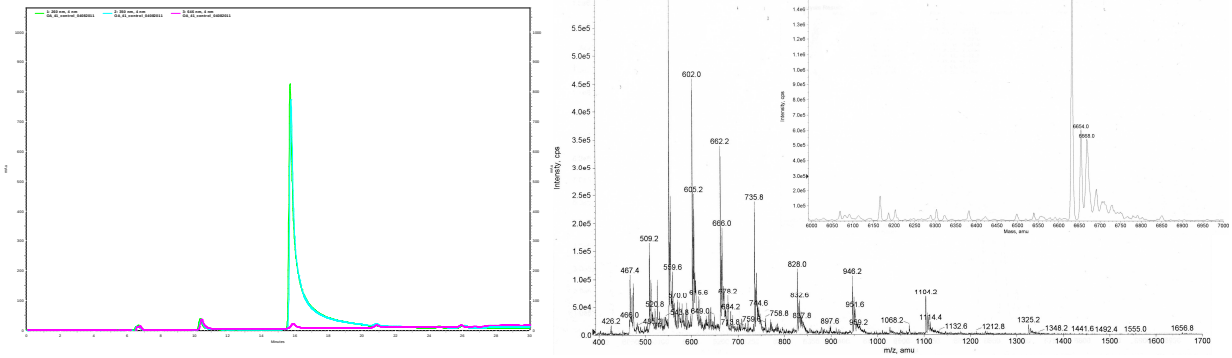


Fig. S9 *(top)* Chromatogram of purified oligomer **9**. Absorbance at 260 nm in green; Absorbance at 350 nm in blue; Absorbance at 646 nm in violet; Eluent A = $(Et_3NH)OAc$ (0.1 M, pH 7.4), Eluent B = MeCN; gradient 5 – 50 % B; t_R = 15.7 min. *(bottom)* ESI-MS of **9** with mass reconstruction; negative ion mode, acetonitrile/H_2O (1:1) + 1 % triethylammonium.

Oligomer **10**

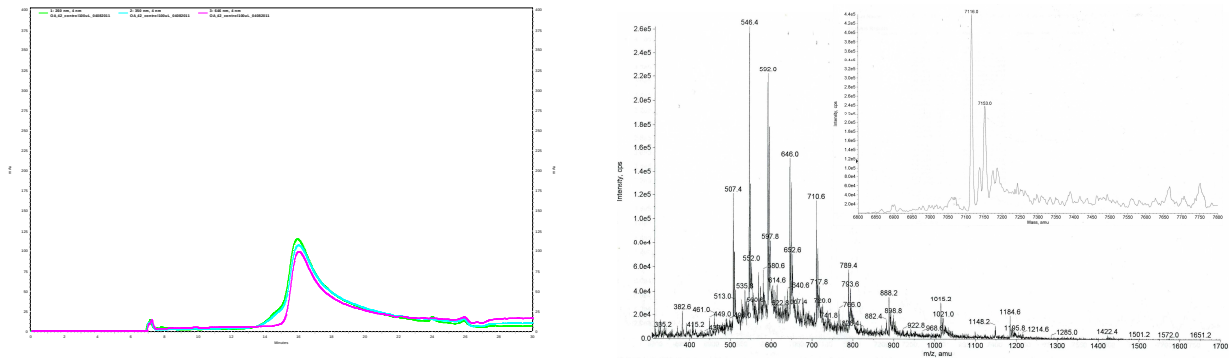


Fig. S10 *(top)* Chromatogram of purified oligomer **10**. Absorbance at 260 nm in green; Absorbance at 350 nm in blue; Absorbance at 646 nm in violet; Eluent A = $(Et_3NH)OAc$ (0.1 M, pH 7.4), Eluent B = MeCN; gradient 5 – 50 % B; t_R = 16.0 min. *(bottom)* ESI-MS of **10** with mass reconstruction; negative ion mode, acetonitrile/H_2O (1:1) + 1 % triethylammonium.

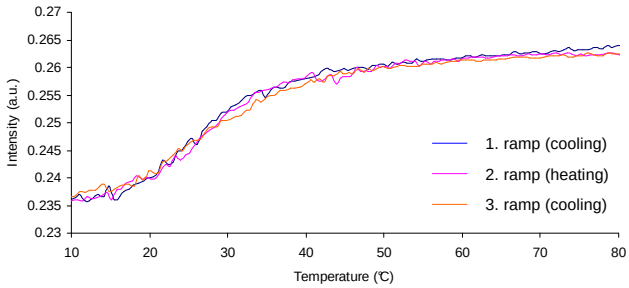
T_m values

Table S2 T_m values of the individual hybrids.

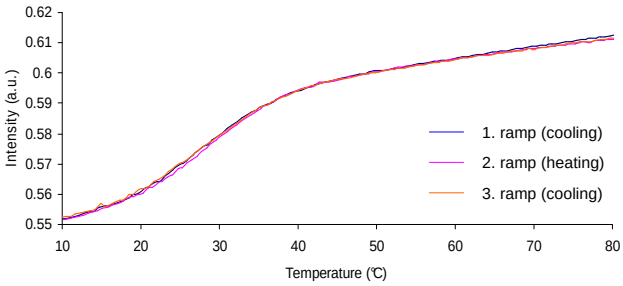
Name	T_m
1*2	25 °C
3*4	28 °C
5*6	31 °C
7*8	33 °C
9*10	34 °C

Thermal denaturation profiles

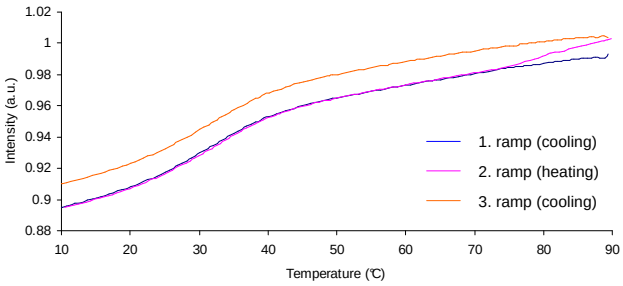
Hybrid **1*2**



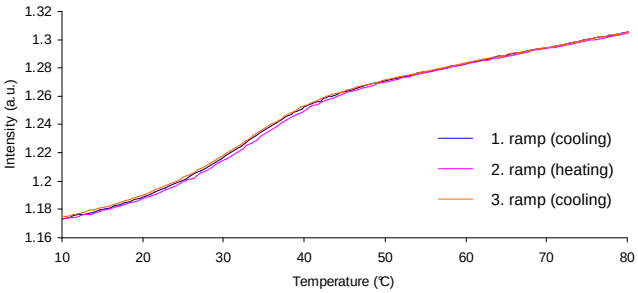
Hybrid **3*4**



Hybrid **5*6**



Hybrid **7*8**



Hybrid **9*10**

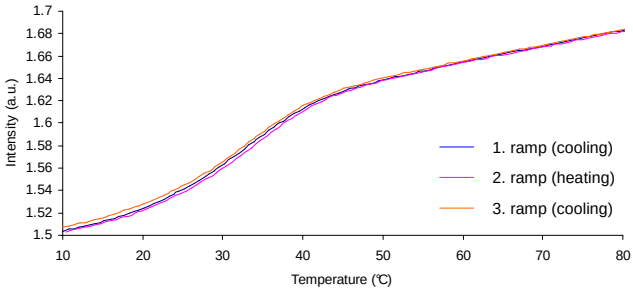
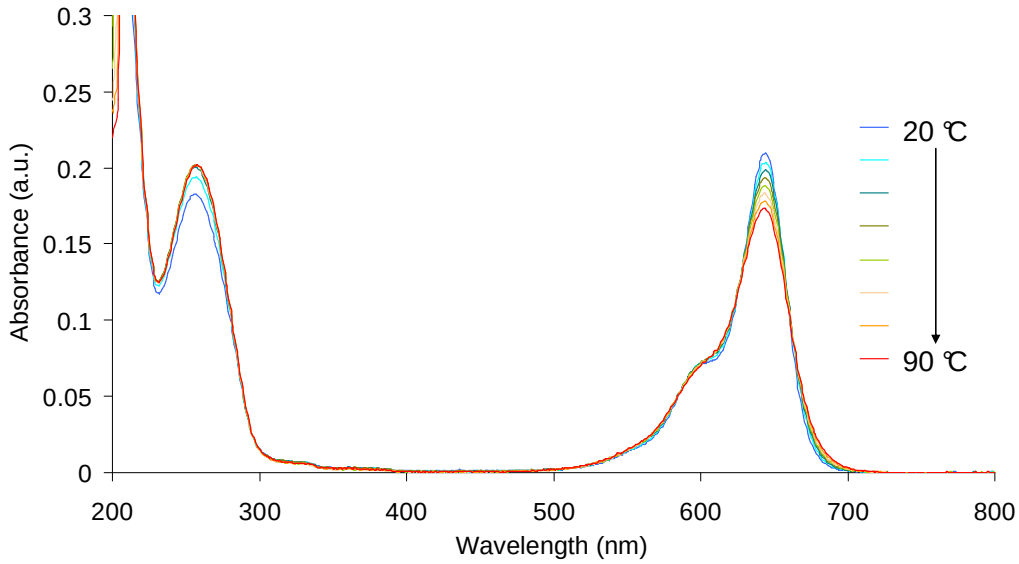


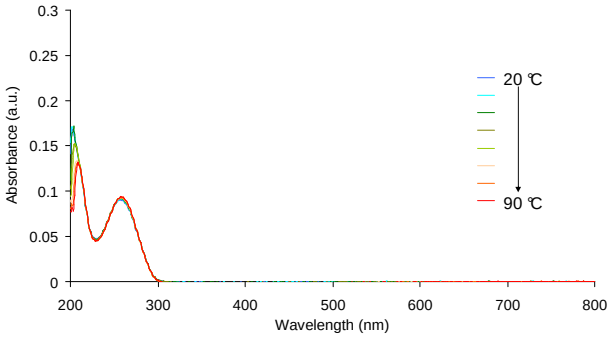
Fig. S11 Melting profiles of hybrids **1*2, 3*4, 5*6, 7*8** and **9*10** with two cooling and one heating ramps (10°C to 90°C). Conditions: 1.0 μM single strand concentration, 100 mM NaCl and 10 mM phosphate buffer (pH = 7.4); temperature gradient 0.5°C/min. The absorption of **1*2** was monitored at 260 nm and **3*4, 5*6, 7*8, 9*10** at 245 nm.

Temperature-dependent UV/Vis measurements

Hybrid **1*2**



Oligomer **1**



Oligomer **2**

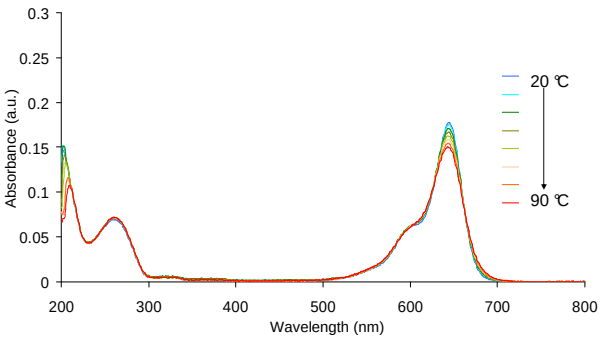
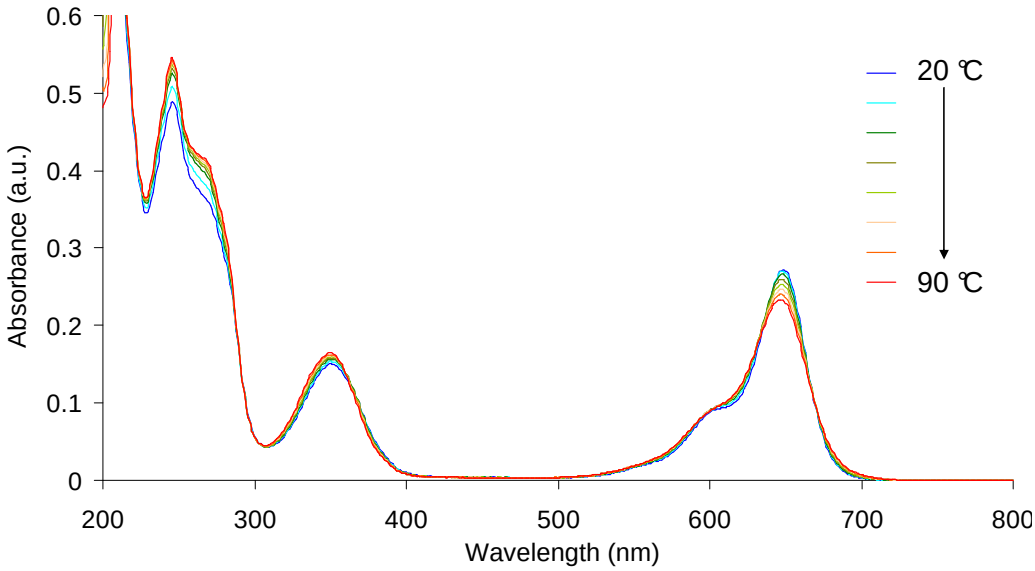
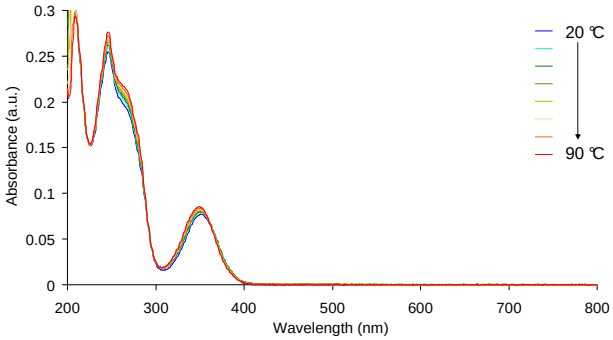


Fig. S12 Temperature-dependent UV/Vis spectra of hybrid **1*2** *(top)*, single strand **1** *(bottom, left)* and single stand **2** *(bottom, right)* Conditions: 1.0 μM single strand concentration, 100 mM NaCl and 10 mM phosphate buffer (pH = 7.4).

Hybrid **3*4**



Oligomer **3**



Oligomer **4**

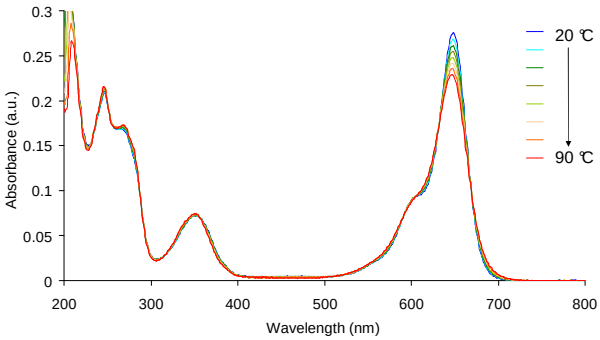
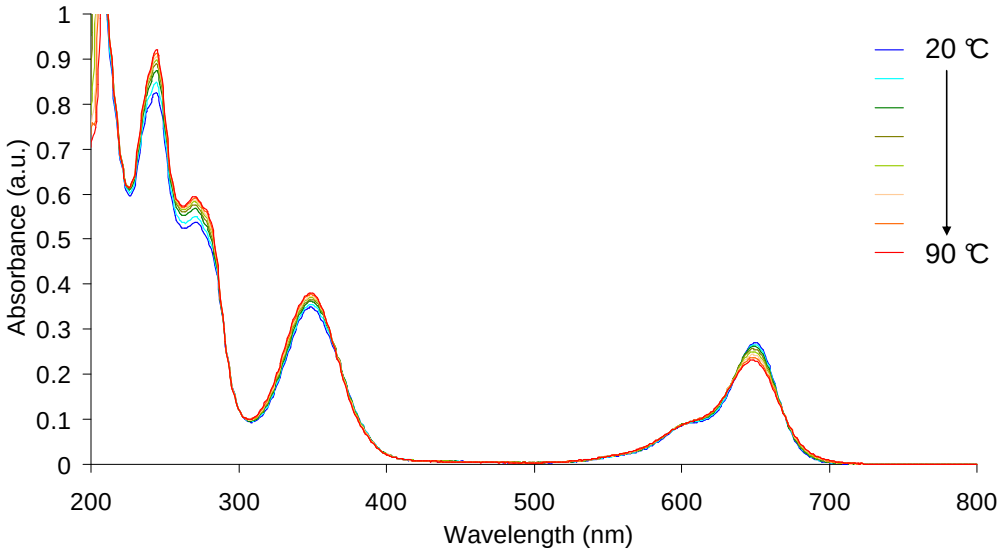
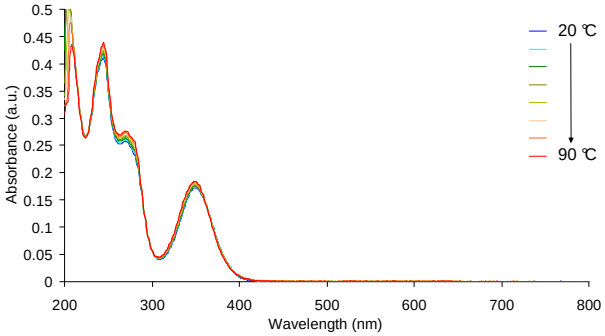


Fig. S13 Temperature-dependent UV/Vis spectra of hybrid **3*4** *(top)*, single strand **3** *(bottom, left)* and single stand **4** *(bottom, right)* Conditions: 1.0 μM single strand concentration, 100 mM NaCl and 10 mM phosphate buffer (pH = 7.4).

Hybrid **5*6**



Oligomer **5**



Oligomer **6**

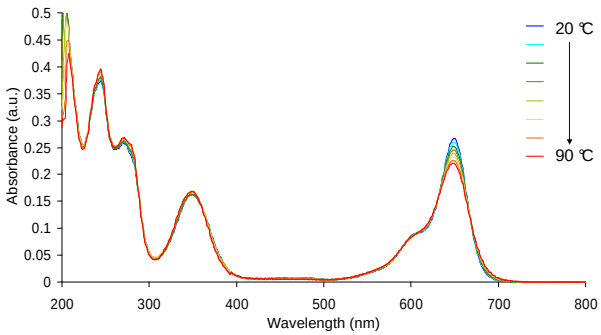
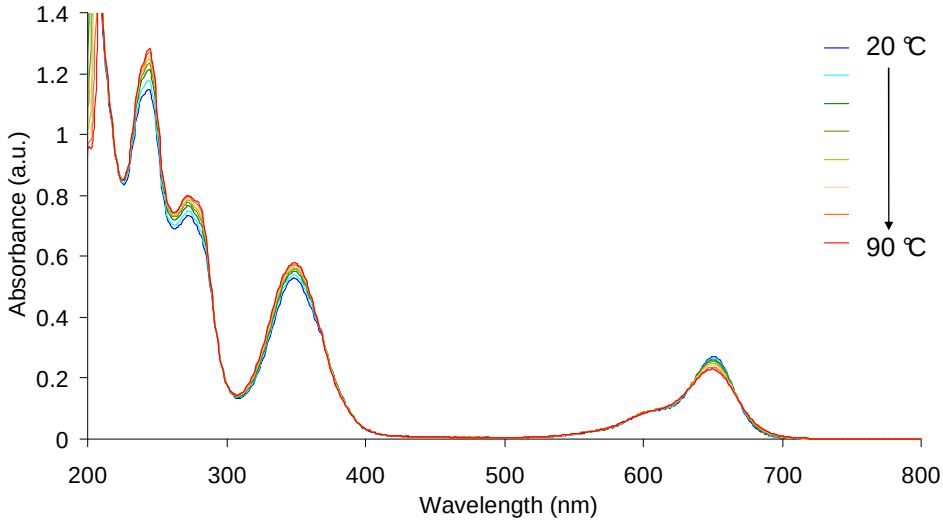
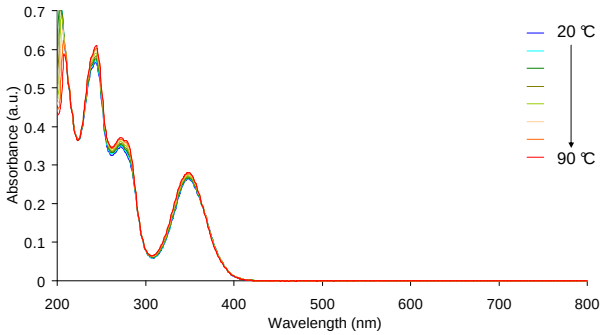


Fig. S14 Temperature-dependent UV/Vis spectra of hybrid **5*6** *(top)*, single strand **5** *(bottom, left)* and single stand **6** *(bottom, right)* Conditions: 1.0 μM single strand concentration, 100 mM NaCl and 10 mM phosphate buffer (pH = 7.4).

Hybrid **7*8**



Oligomer **7**



Oligomer **8**

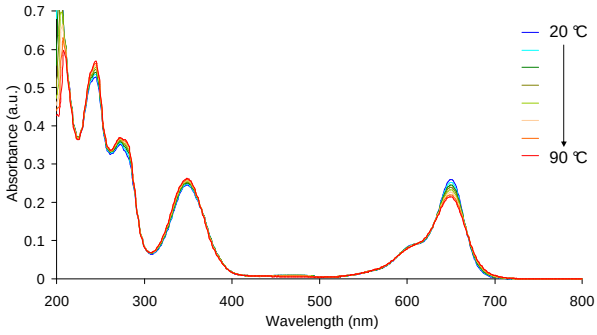
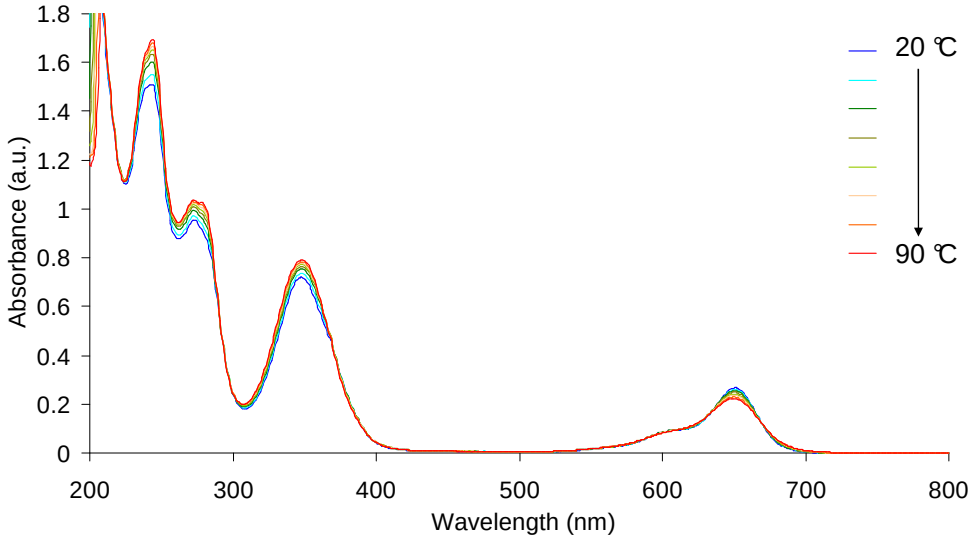
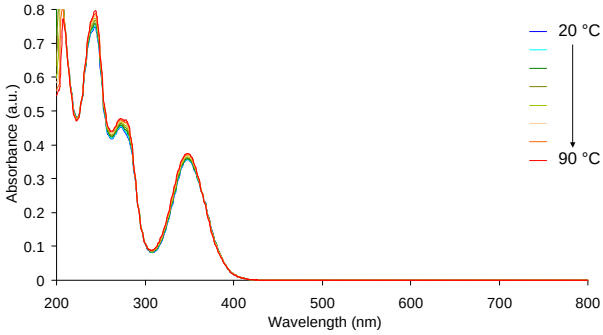


Fig. S15 Temperature-dependent UV/Vis spectra of hybrid **7*8** *(top)*, single strand **7** *(bottom, left)* and single stand **8** *(bottom, right)* Conditions: 1.0 μM single strand concentration, 100 mM NaCl and 10 mM phosphate buffer (pH = 7.4).

Hybrid **9*10**



Oligomer **9**



Oligomer **10**

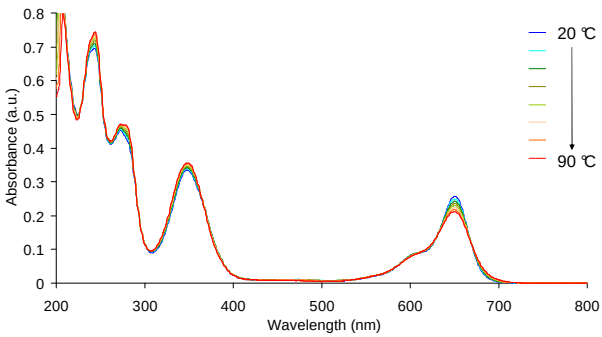


Fig. S16 Temperature-dependent UV/Vis spectra of hybrid **9*10** *(top)*, single strand **9** *(bottom, left)* and single stand **10** *(bottom, right)* Conditions: 1.0 μM single strand concentration, 100 mM NaCl and 10 mM phosphate buffer (pH = 7.4).

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Fluorescence measurements with adjusted pyrene absorption: emission spectra

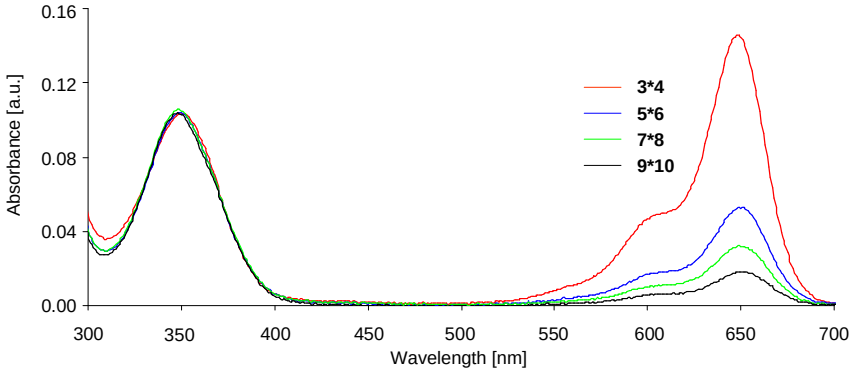
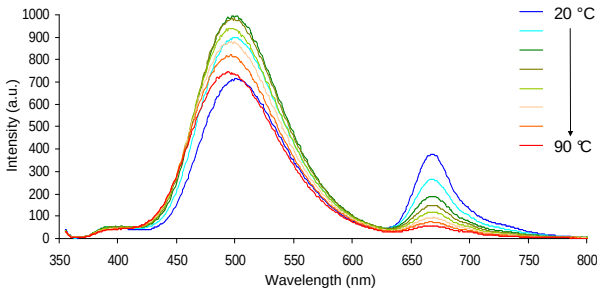
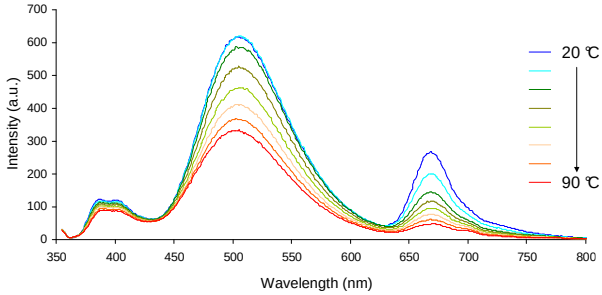


Fig. S17 Absorbance spectra of hybrids **3*4, 5*6, 7*8** and **9*10** with adjusted pyrene absorption (350nm) Conditions: 10 mM sodium phosphate buffer pH 7.4 and 100 mM NaCl at 20°C (see S3).

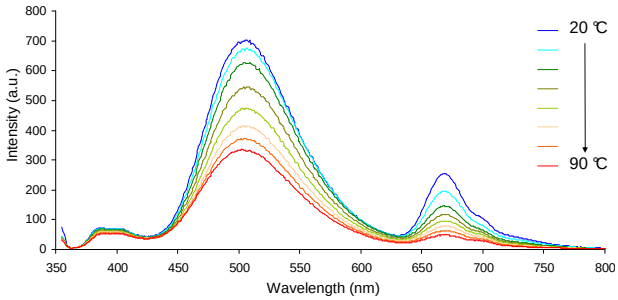
Hybrid **3*4**



Hybrid **5*6**



Hybrid **7*8**



Hybrid **9*10**

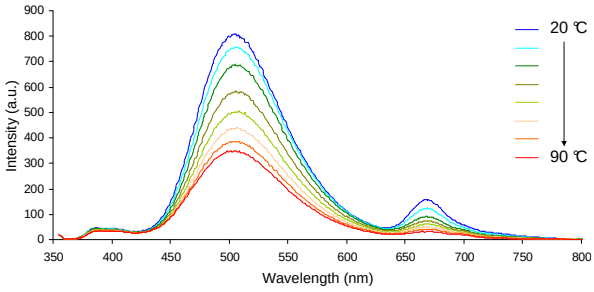


Fig. S18 Temperature-dependent emission spectra of hybrids **3*4, 5*6, 7*8** and **9*10** with adjusted pyrene absorption. Conditions: 10 mM sodium phosphate buffer (pH 7.4), 100 mM NaCl at 20°C, λ_{ex}: 350 nm, ex/em slit widths: 5/10 nm; for concentrations of oligomers see S3.

Fluorescence measurements with adjusted pyrene absorption: excitation spectra

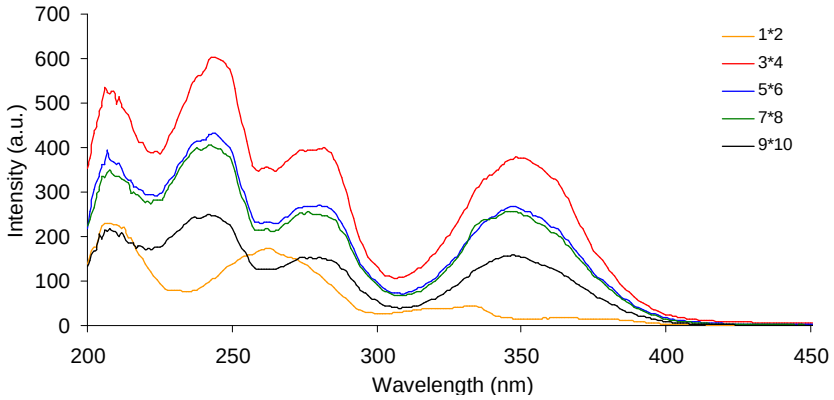


Fig. S19 Temperature-dependent excitation spectra of **1*2**, **3*4**, **5*6**, **7*8**, **9*10**, respectively, with adjusted pyrene absorption (350 nm). Conditions: adjusted single strand concentration, 100 mM NaCl and 10 mM phosphate buffer (pH = 7.4), λ_{em}: 670 nm, ex/em slit widths: 5/5 nm.

UV/Vis spectra (1.0 µM Cy5); all hybrids, 20 °C

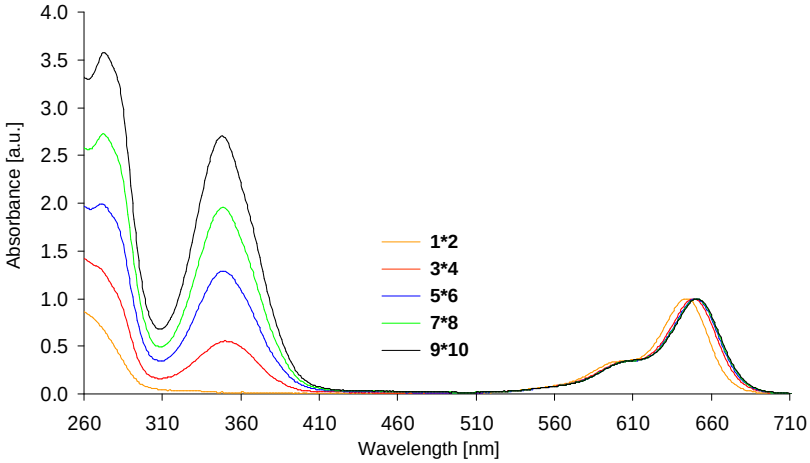
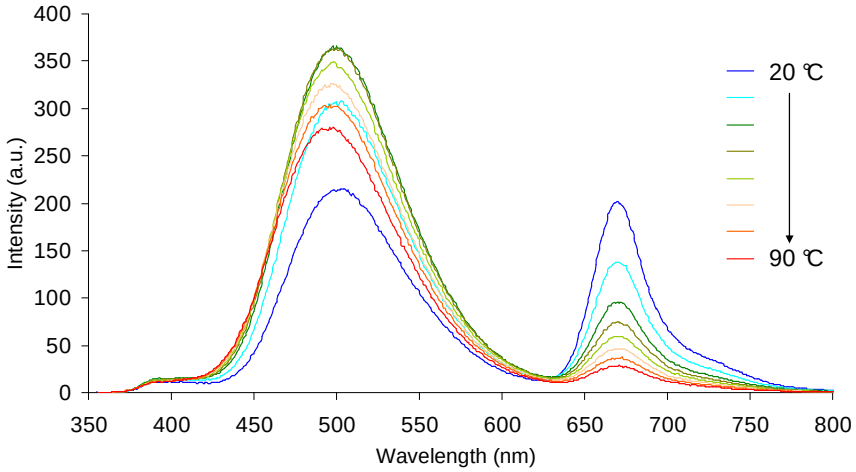


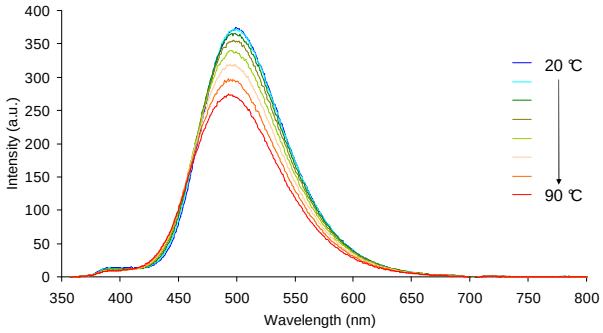
Fig. S20 Absorbance spectra of hybrids **1*2**, **3*4**, **5*6**, **7*8** and **9*10** at 1.0 µM concentration. Conditions: 10 mM sodium phosphate buffer, pH 7.4, 100 mM NaCl at 20°C.

Fluorescence measurements (1.0 μM Cy5): emission spectra

Hybrid **3*4**



Oligomer **3**



Oligomer **4**

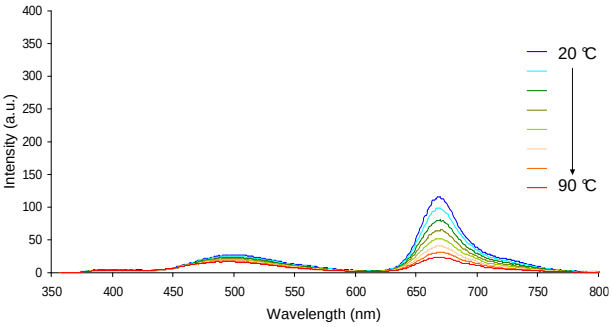
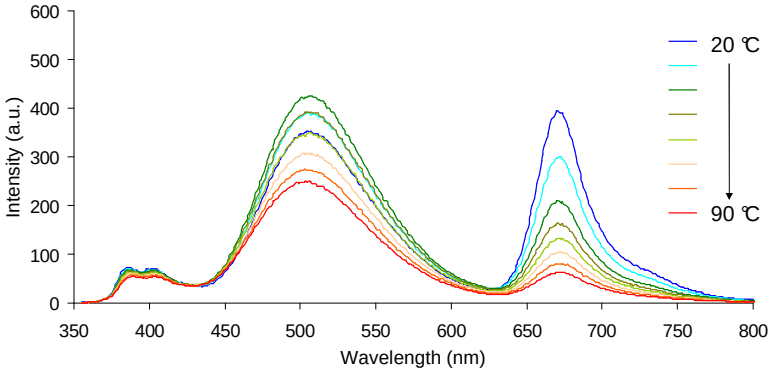
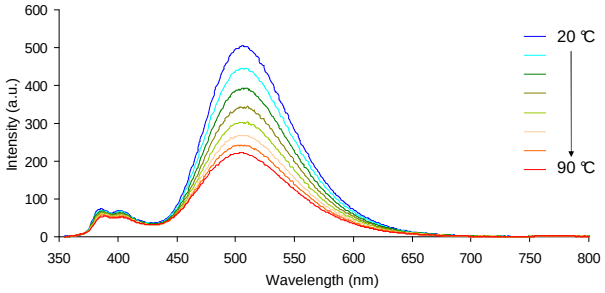


Fig. S21 Temperature-dependent emission spectra of hybrid **3*4** *(top)*, single strand **3** *(bottom left)* and single strand **4** *(bottom right)*. Conditions: 1.0 μM single strand concentration, 100 mM NaCl and 10 mM phosphate buffer (pH = 7.4), λ_{ex}: 350 nm, ex/em slit widths: 5/5 nm.

Hybrid **5*6**



Oligomer **5**



Oligomer **6**

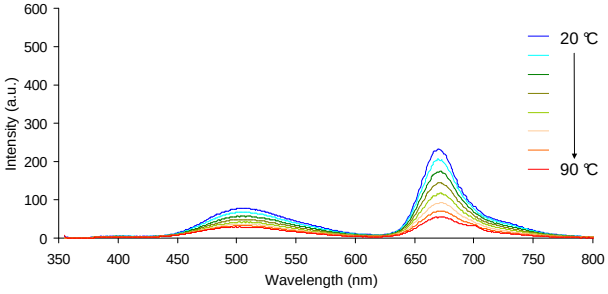
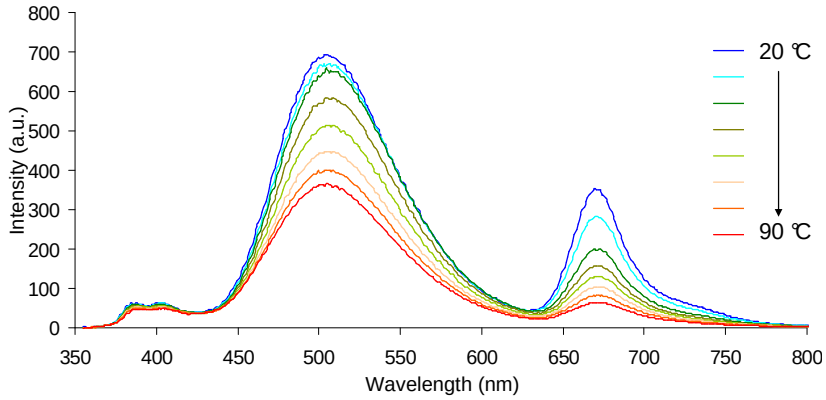
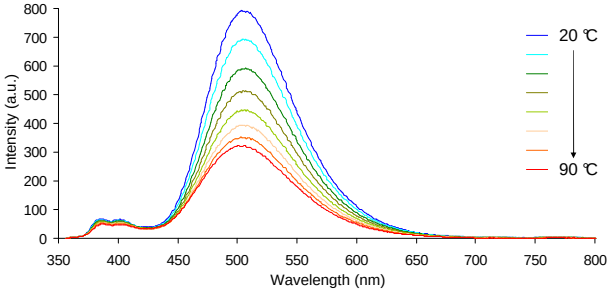


Fig. S22 Temperature-dependent emission spectra of hybrid **5*6** *(top)*, single strand **5** *(bottom left)* and single strand **6** *(bottom right)*. Conditions: 1.0 μM single strand concentration, 100 mM NaCl and 10 mM phosphate buffer (pH = 7.4), λ_{ex}: 350 nm, ex/em slit widths: 5/5 nm.

Hybrid **7*8**



Oligomer **7**



Oligomer **8**

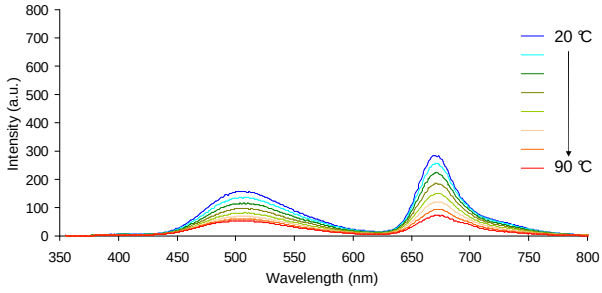
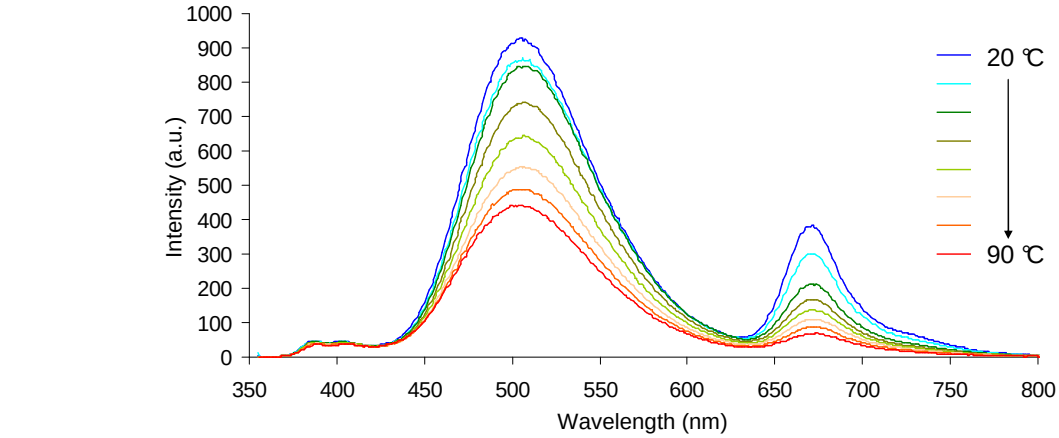
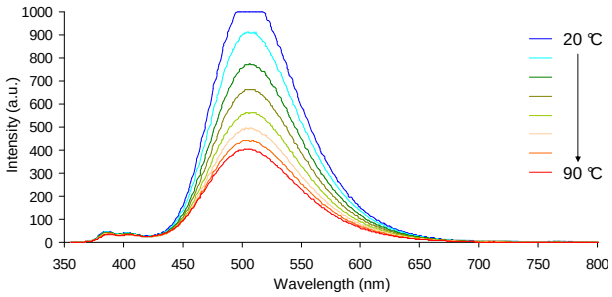


Fig. S23 Temperature-dependent emission spectra of hybrid **7*8** *(top)*, single strand **7** *(bottom left)* and single strand **8** *(bottom right)*. Conditions: 1.0 μM single strand concentration, 100 mM NaCl and 10 mM phosphate buffer (pH = 7.4), λ_{ex}: 350 nm, ex/em slit widths: 5/5 nm.

Hybrid **9*10**



Oligomer **9**



Oligomer **10**

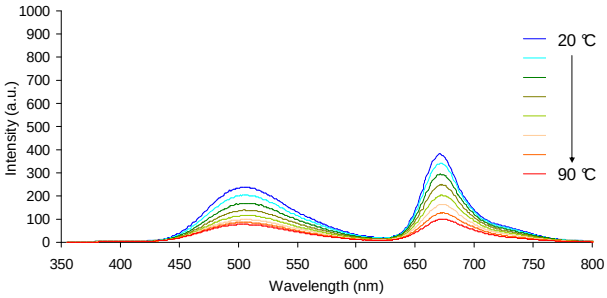


Fig. S24 Temperature-dependent emission spectra of hybrid **9*10** *(top)*, single strand **9** *(bottom left)* and single strand **10** *(bottom right)*. Conditions: 1.0 μM single strand concentrations, 100 mM NaCl and 10 mM phosphate buffer (pH = 7.4), λ_{ex}: 350 nm, ex/em slit widths: 5/5 nm.

Fluorescence measurements (1.0 μM Cy5): excitation spectra

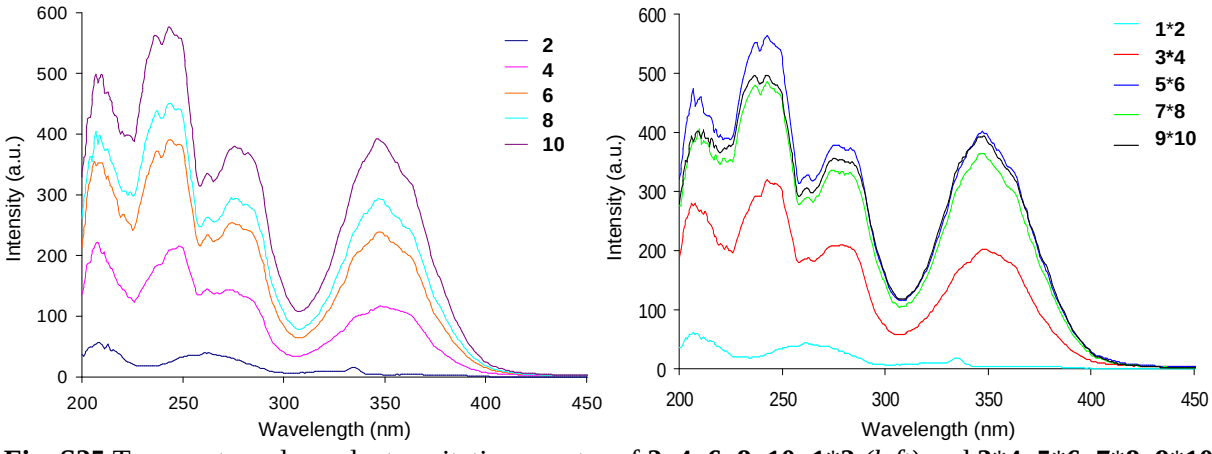


Fig. S25 Temperature-dependent excitation spectra of **2**, **4**, **6**, **8**, **10**, **1*2** *(left)* and **3*4**, **5*6**, **7*8**, **9*10** *(right)*. Conditions: 1.0 μM single strand concentration, 100 mM NaCl and 10 mM phosphate buffer (pH = 7.4). λ_{em}: 670 nm, ex/em slit widths: 5/5 nm.

Modelling of hybrid 3*4

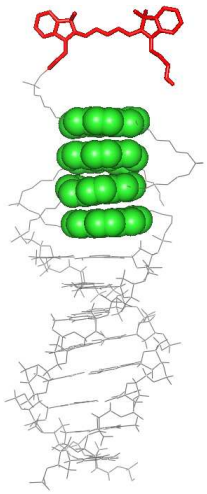


Fig. S26 Illustration of a molecular model of hybrid **3*4** based on *Abalone*, molecular modeling software. DNA (grey), four 1,8-dicarboxamide pyrenes (green) and a Cy5 acceptor (red).

Quantum yield determination

Quantum yield determination was performed for oligomer **3** and oligomer **5** with quinine sulfate as a reference. UV/Vis spectra were collected in the range of 200 nm – 500 nm (20°C). Oligonucleotide concentration was adjusted to keep the absorption between 0.05 - 0.1 a.u. Samples were measured in 100 mM NaCl and 10 mM sodium phosphate buffer (pH 7.4). The quinine sulfate concentration was set to approx. $5x10^{-6}$ M in 0.05 M H_2SO_4. Fluorescence data were collected in a range of 355 nm – 700 nm, λ_{ex} was 350 nm in all experiments. The quantum yields were calculated using the following equation:

$$\Phi_{ref} = \frac{I_{comp} \bullet Abs_{ref}}{Abs_{comp} \bullet I_{ref}} \quad \Phi_{ref}$$

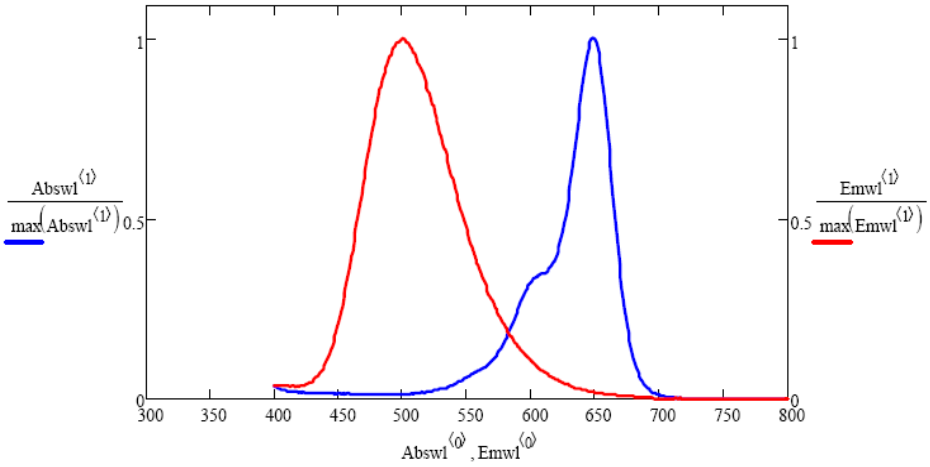
where I_{comp} is the area of the fluorescence signal under the curve of the compound, Abs_{comp} is the intensity of the absorbance at 350 nm of the compound, I_{ref} is the area under the curve of quinine sulfate, Abs_{ref} is the intensity of the absorbance at 350 nm of quinine sulfate and Φ_{ref} is the quantum yield of quinine sulfate (0.546).[4]

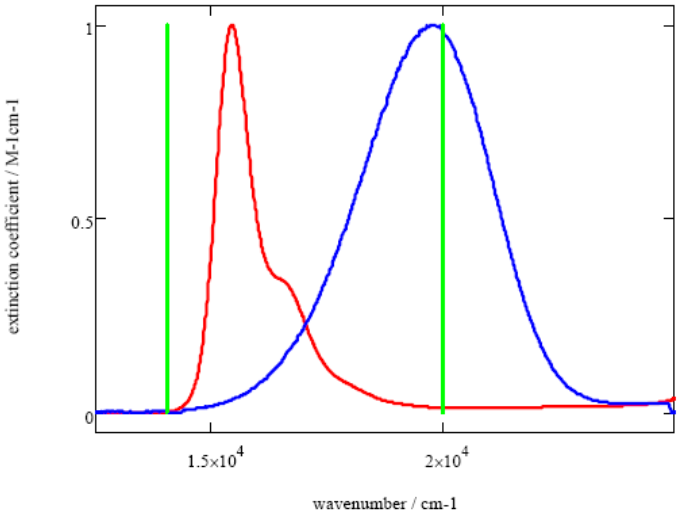
Table S3 Quantum yield Φ_{pyrene} determination.

Oligomer	Quantum yield Φ_{pyrene}
3	0.2614
5	0.1770

[4] S. Werder, V. L. Malinovskii, R. Häner *Org. Lett.* 2008, **10**, 2011-2014.

Performed Calculations I





Spectral overlap integral (calculated):

$j_{overl} = 1.363 \times 10^{-13} \cdot \frac{L \cdot cm^3}{mol}$

$J_{overl} = 1.363 \times 10^{-10} \cdot \frac{cm^6}{mol}$

Oscillator strength of Cy5, calculated:

$f_{osc} = 1.604$

For calculating the Förster radius R_0 we need:
information on the quantum yield for fluorescence of the donor ϕ_D,
the refraction index n in the specific solvent
and the orientation factor κ^2 (for isotropic conditions 2/3).
N_A is the Avogadro-number.

$\phi := 0.2$

$n_{refindex} := 1.33$ (refractive index of water)

$\kappa 2 := \frac{2}{3}$

$$R_0 := \left(J_{overl} \cdot \frac{9 \cdot \ln(10) \cdot \phi \cdot \kappa 2}{128 \cdot \pi^5 \cdot n_{refindex}^4 \cdot N_A} \right)^{\frac{1}{6}}$$

Förster Radius (calculated)

$R_0 = 4.149\,nm$

If a luminescence quantum yield of 0.18 for the pyrene exciplex is used, a Förster radius of 4.077 is obtained.
Hence, we decided to use R_0 = 4.1 nm.
We have further used ΔR = 0.35 nm for the distance between the pyrene molecules.

Performed Calculations II: Absorption[5]

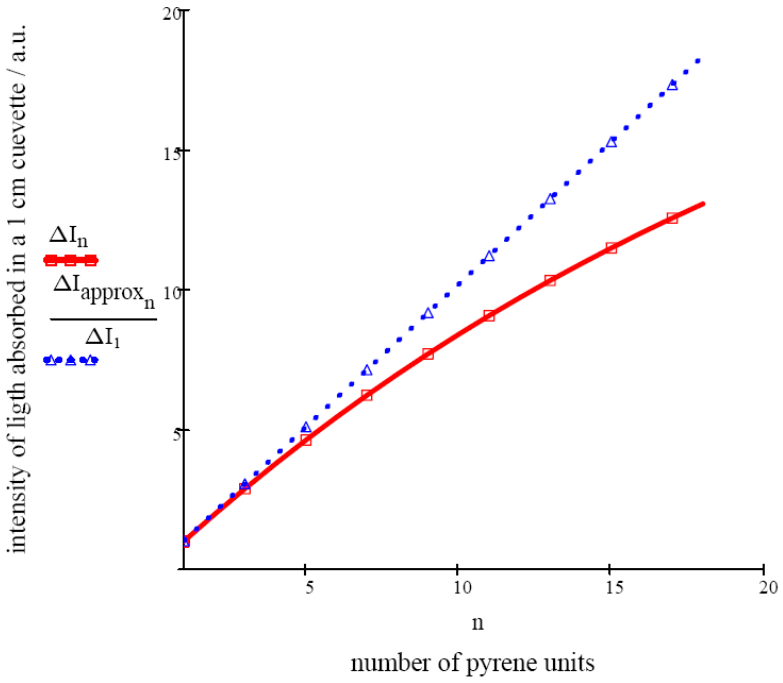
ORIGINE ≡ 1 $\quad dm := 0.1m$

Intensity of absobed light in a cuvette of 1 cm length.

$I_0 := 1$ $\quad \varepsilon := 35 \cdot 10^3 \frac{L}{mol \cdot cm}$ $\quad c := 10^{-6} \frac{mol}{L}$ $\quad d := 1cm$

$n := 1 .. 18$ $\quad c_n := \frac{1}{2} \cdot n \cdot c$ $\quad \Delta I_n := 1 - 10^{-\varepsilon \cdot d \cdot c_n}$ $\quad \Delta I_{approx_n} := 2.3 \cdot \varepsilon \cdot d \cdot c_n$

Skalierung: $\quad Scal := \Delta I_1$ $\quad \Delta I_n := \frac{\Delta I_n}{Scal}$ $\quad \Delta I_{approx_n} := \frac{\Delta I_{approx_n}}{Scal}$

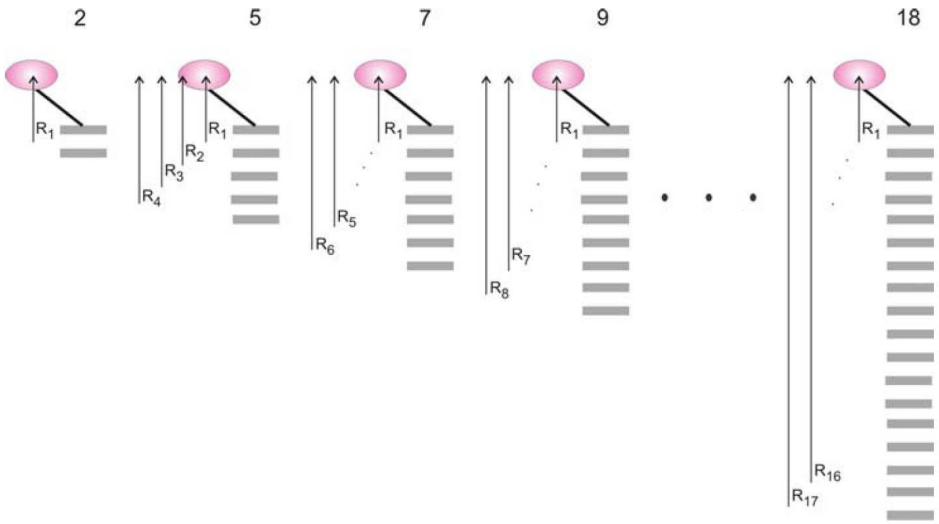


This graph shows, that the amount of light absobed light by the pyrene is not linear with repect to the number of pyrene molecules in a composit.

Intensity of the Luminescence in absence of Cy5 (pure eximer emission):

$factor := 1$ $\quad \Phi_{Excim} := 1$ $\quad IF_{Excim_n} := factor \cdot \Phi_{Excim} \cdot \Delta I_n$

$IF_{ExcimApprox_n} := factor \cdot \Phi_{Excim} \cdot \Delta I_{approx_n}$



$R_0 := 4.1\text{nm}$ $\Delta R := 0.35\text{nm}$ $J := 1 .. 17$ $Jn := 2 .. 18$

$$P := \frac{1}{1 + \left(\frac{R}{R_0}\right)^6}$$

$$\text{ProbP}(R_0, R_1, J) := \left[1 + \left[\frac{R_1}{R_0} + (J-1)\cdot\frac{\Delta R}{R_0}\right]^6\right]^{-1}$$

$$\text{SUMPP}(R_0, R_1, Jn) := \frac{1}{Jn-1}\cdot\sum_{i=1}^{Jn-1} \text{ProbP}(R_0, R_1, i)$$

$$\text{SUMProbP}(R_0, R_1, Jn) := \text{SUMPP}(R_0, R_1, Jn)\cdot\Delta I_{Jn}$$

[5] G. Calzaferri, A. Devaux, *in Supramolecular Photochemistry - Controlling Photochemical Processes, Eds.:* V. Ramamurthy, Y. Inoue, John Wiley & Sons, New Jersey,US, 2011,*Chapter 9, pp. 285-387.*

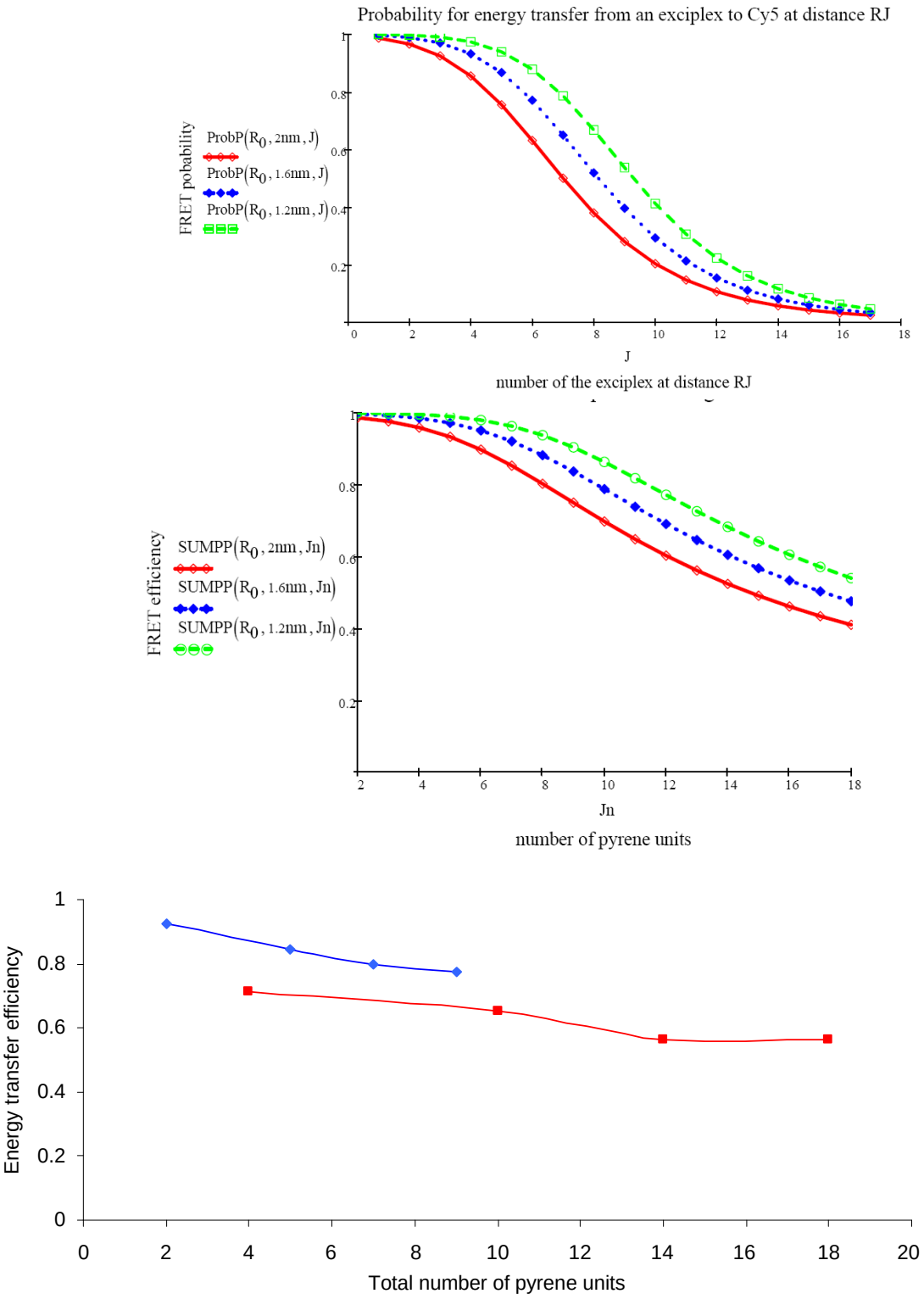


Fig. S27 Development of energy transfer efficiencies of single strands (blue) and hybrids (red) with an increasing number of donor residues.

Performed Calculations III: Experimental and theoretical fluorescence emission of Cy5

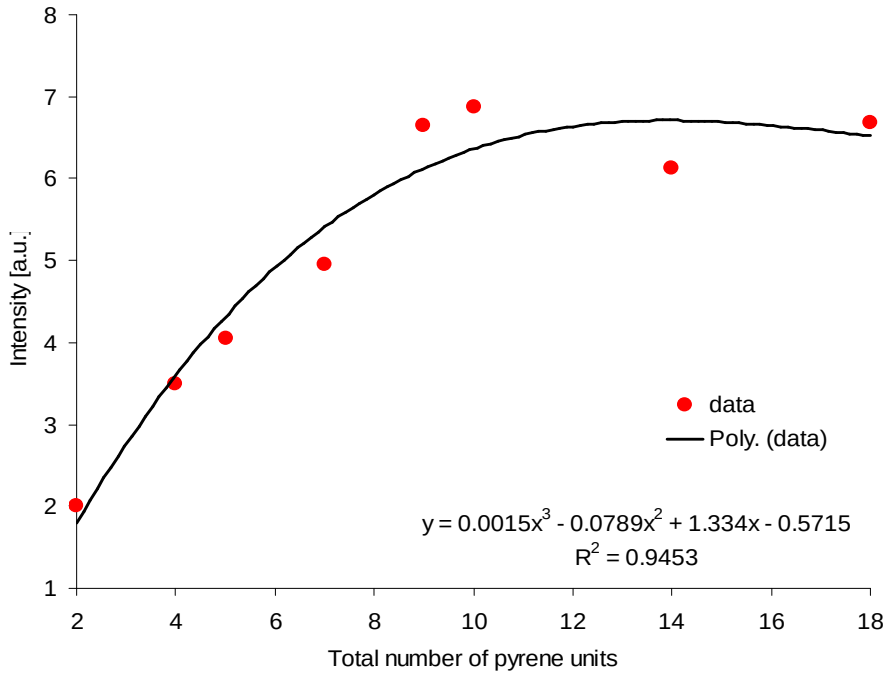


Fig. S28 Experimental fluorescence emission of Cy5 upon excitation of pyrene (data) and the corresponding trend line (polynomial) with equation and correlation coefficient R^2.

$JN := 0 .. 16 \qquad ind_{JN} := JN + 2 \qquad M2nm^{\langle 0 \rangle} := ind \qquad M1\_6nm^{\langle 0 \rangle} := ind \qquad M1\_2nm^{\langle 0 \rangle} := ind$

$val2nm_{JN} := SUMProbP\left(R_0, 2nm, JN + 2\right) \qquad M2nm^{\langle 1 \rangle} := val2nm$

$val1\_6nm_{JN} := SUMProbP\left(R_0, 1.6nm, JN + 2\right) \qquad M1\_6nm^{\langle 1 \rangle} := val1\_6nm$

$val1\_2nm_{JN} := SUMProbP\left(R_0, 1.2nm, JN + 2\right) \qquad M1\_2nm^{\langle 1 \rangle} := val1\_2nm$