Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Supplemental Material of

Photophysical characterization of oligopyrene modules for DNA-based nanosystems

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In a variety of applications, fluorescence decay can be adequately approximated by a sum of exponentials

$$I(t) = \sum_{k=1}^{n} A_k \exp(-t/\tau_k),$$

where n is the number of exponentials; A_k and τ_k (k=1,..,n) are, respectively, the amplitudes and decay constants which have to be defined. Using this sum as model function we obtain values presented in Table S1.

Picosecond resolution enables us to apply a global fitting procedure with above mentioned model functions and find excimer emission rise time (Table S2). In the global analysis, monomer and excimer kinetics are combined in a data set and simultaneously fitted. Two decay constants are linked, what makes them equal for both functions in a set. Several nanosecond decay constants are fixed into the predefined values from Table S1 as determined there more accurately.

Table S1. Lifetimes and amplitudes from multiexponential fitting of ns-scaled decay kinetics

	τ_1, ns (A_1)	τ_2, ns (A_2)	τ_3, ns (A_3)
ss1			
monomer [a,b,c]	6.66 (1.62)	1.68 (1.97)	
ds1			
monomer [b,d,e]	7.17 (1.47)	1.66 (1.75)	
excimer [b,e,f]	20.68 (0.90)	6.30 (1.33)	
ss2			
monomer [g,h,i]	9.07 (0.40)	2.18 (1.10)	0.45 (3.01)
excimer [b,j,k]	34.42 (4.93)	9.65 (6.36)	
ds2			
monomer [g,h,i]	9.32 (0.80)	1.83 (2.29)	0.22 (6.88)
excimer [b,j,k]	35.78 (14.47)	9.44 (8.25)	
ss3			
monomer [g,h,i]	11.64 (0.49)	2.71 (1.24)	0.50 (3.18)
excimer [b,j,k]	38.86 (6.71)	11.30 (3.89)	
ds3			
monomer [g,h,i]	11.85 (0.54)	2.97 (1.47)	0.47 (3.80)
excimer [b,j,k]	36.37 (6.13)	12.82 (4.46)	
ss4			
monomer [g,h,l]	17.48 (0.99)	3.12 (1.95)	0.35 (5.05)
excimer [f,h,l]	37.56 (9.60)	9.71 (2.59)	1.52 (1.58)
ds4			
monomer [g,h,l]	17.12 (1.01)	4.21 (1.28)	0.63 (2.43)
excimer [f,h,l]	37.76 (4.43)	11.51 (1.40)	1.74 (0.94)
ss5			
monomer [g,h,l]	13.42 (1.30)	2.25 (1.93)	0.28 (5.56)
excimer [f,h,l]	38.27 (12.14)	9.93 (3.61)	1.60 (2.16)
ds5			
monomer [g,h,l]	17.10 (0.58)	4.04 (0.89)	0.85 (1.54)
excimer [f,h,l]	36.53 (3.94)	9.32 (1.13)	1.51 (0.73)
ss6			

monomer [g,h,l]	13.68 (1.75)	2.69 (2.02)	0.32 (5.36)
excimer [f,h,l]	38.19 (14.08)	4.47 (3.00)	
ds6			
monomer [g,h,l]	17.86 (0.70)	4.41 (1.02)	0.55 (2.25)
excimer [f,h,l]	35.01 (3.26)	4.82 (0.85)	
ss7			
monomer [g,h,i]	11.84 (0.91)	2.73 (2.05)	0.23 (5.16)
excimer [b,j,k]	37.62 (6.74)	12.80 (3.00)	
ds7			
monomer [g,h,i]	12.32 (1.14)	2.58 (1.95)	0.22 (4.93)
excimer [b,j,k]	36.21 (6.67)	13.32 (3.27)	

[a]Registration wavelength 405 nm, [b]Excitation wavelength 337 nm, [c]Time resolution 38.3 ps/ channel, [d]Registration wavelength 395 nm, [e]Time resolution 76.2 ps/ channel, [f]Registration wavelength 520 nm, [g]Registration wavelength 390 nm, [h]Excitation wavelength 298 nm, [i]Time resolution 20.6 ps/ channel, [j]Registration wavelength 540 nm, [k]Time resolution 212.3 ps/ channel, [l]Time resolution 41.2 ps/ channel.

Table S2. Lifetimes and amplitudes from multiexponential global fitting of ps-scaled decay kinetics at excitation wavelength 298 nm

	τ_1, ns (A_1)	τ_2, ns (A_2)	τ_3, ps (A_3)	τ_4, ps (A_4)
ds1				
monomer [a,b]	7.17 [c] (5.09)	1.66 [c] (9.41)	160 (12.67)	**4.22**[d] (110.1)
excimer [b,e]	20.68 [c] (2.61)	6.30 [c] (21.42)	310 (7.55)	**4.22**[d] (-58.6)
ss2				
monomer [f,g]	9.07[c] (2.38)	0.27 (7.50)	**52.95**[d] (11.20)	0.25 (1690)
excimer [e,g]	34.42[c] (0.0002)	9.65[c] (26.20)	**52.95**[d] (-7.46)	
ds2				
monomer [f,g]	9.32[c] (3.50)	0.17 (9.89)	**40.97**[d] (9.97)	2.29 (219.7)
excimer [e,g]	35.78[c] (3.26)	9.44[c] (23.12)	**40.97**[d] (-6.82)	
ss3				
monomer [f,g]	11.64[c] (2.94)	0.25 (7.75)	**44.47**[d] (17.24)	0.03 (1730)
excimer [g,h]	38.86[c] (17.30)	11.30[c] (8.33)	**44.47**[d] (-8.20)	
ds3				
monomer [f,g]	11.85[c] (1.66)	0.55 (6.24)	**60.79**[d] (15.57)	1.16 (459.3)
excimer [g,h]	36.37[c] (0.003)	12.82[c] (26.08)	**60.79**[d] (-5.93)	
ss4				
monomer [b,f]	17.48[c] (3.36)	0.38 (8.31)	**29.20**[d] (35.33)	0.21 (12.5)
excimer [b,e]	37.56[c] (2.27)	9.71[c] (23.74)	**29.20**[d] (-0.45)	
ds4				
monomer [b,f]	17.12[c] (5.14)	0.51 (7.56)	**67.62**[d] (13.87)	2.95 (147.4)
excimer [b,e]	37.76[c] (0.008)	11.51[c] (26.79)	**67.62**[d] (-0.48)	
ss5				
monomer [b,f]	13.42[c] (2.83)	0.40 (6.46)	**48.79**[d] (15.86)	0.07 (1180)
excimer [b,e]	38.27[c] (0.0003)	9.93[c] (26.44)	**48.79**[d] (-1.00)	
ds5				
monomer [b,f]	17.10[c] (2.84)	0.47 (5.70)	**60.46**[d] (15.94)	4.07 (131.0)
excimer [b,e]	36.53[c] (0.0019)	9.32[c] (27.58)	**60.46**[d] (-0.51)	
ss6				
monomer [b,f]	13.68[c] (3.27)	0.56 (5.63)	**65.83**[d] (14.12)	0.92 (545.7)
excimer [b,e]	38.19[c] (17.48)	4.47[c] (7.53)	**65.83**[d] (-0.94)	
ds6				
monomer [b,f]	17.86[c] (3.64)	0.46 (5.96)	**60.52**[d] (15.17)	5.62 (79.4)
excimer [b,e]	35.01[c] (13.66)	4.82[c] (12.78)	**60.52**[d] (-0.95)	
ss7				
monomer [f,g]	11.84[c] (2.45)	0.48 (4.05)	**54.31**[d] (14.32)	0.78 (733.7)
excimer [g,h]	37.62[c] (0.0035)	12.80[c] (25.98)	**54.31**[d] (-4.43)	
ds7				
monomer [f,g]	12.32[c] (4.16)	0.22 (6.72)	**40.22**[d] (13.51)	0.03 (2260)
excimer [g,h]	36.21[c] (0.0003)	13.32[c] (26.52)	**40.22**[d] (-8.26)	

[a]Registration wavelength 395 nm, [b]Time resolution 1.025 ps/ channel, [c]Fixed parameter (taken from Table S1), [d]Linked parameters in simultaneous monomer-excimer fitting procedure, [e]Registration wavelength 520 nm, [f]Registration wavelength 390 nm, [g]Time resolution 0.512 ps/ channel, [h]Registration wavelength 540 nm.