Time-Resolved Transient Optical Absorption Study of Bis(terpyridyl)oligothiophenes and Their Metallo-Supramolecular Polymers with Zn(II) Ion Couplers

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SUPPORTING INFORMATION

Time-resolved photoluminescence measurements.

Fluorescence decay was monitored with a FluoroHub single photon counting controller on a Fluorolog 3-22 Jobin Yvon Spex instrument using excitation at λ_{ex} 472 nm. The respective DMSO solutions were at concentration 10⁻⁴M. The free ligands were measured at single wavelength, the dynamers were measured at three different wavelengths (530 or 539, 600 and 700 nm, respectively). The obtained kinetic traces recorded at the indicated wavelength were

fitted with two- and three- exponential decays in case of free ligands and dynamers, respectively.

The resulting lifetimes of photoluminescence decays are summarized in Table S1.

Table S1: Summary of the photoluminescence lifetimes found in the studied solutions. The obtained lifetimes and their respective standard errors are given in seconds.

Т	(in sec)			
			fract.	
	530 nm	S. Dev	(%)	
T1	5.47E-10	1.47E-11	95.67	
T2	1.35E-09	8.34E-11	4.33	
X^2	1.424818			

PT (in sec)

			fract.			fract.			fract.
	530 nm	S. Dev	(%)	600 nm	S. Dev	(%)	700 nm	S. Dev	(%)
T1	8.65E-10	2.63E-11	59.45	4.50E-10	1.14E-11	24.55	7.64E-10	1.10E-10	44.85
T2	2.01E-10	6.70E-12	22.39	1.04E-09	3.51E-11	69.79	1.17E-09	7.05E-11	54.08
Т3	1.52E-09	4.47E-11	18.17	1.77E-09	3.61E-11	5.66	2.80E-09	1.30E-09	1.07
X^2	1.277786			1.537482			1.978503		

T16 (in sec)

			fract.	
	530 nm	S. Dev	(%)	
T1	3.80E-10	2.65E-11	40.73	
T2	7.26E-10	7.97E-12	59.27	
X^2	1.473183			

PT16 (in sec)

			fract.			fract.			fract.
	539 nm	S. Dev	(%)	600 nm	S. Dev	(%)	700 nm	S. Dev	(%)
T1	4.71E-11	1.06E-11	17.5	2.15E-10	1.16E-11	25.79	2.81E-10	1.02E-11	44.15
T2	5.61E-10	7.08E-12	55.47	7.65E-10	1.71E-11	48.7	9.04E-10	2.85E-11	37.62
T3	2.41E-09	2.27E-11	27.02	2.26E-09	2.54E-11	25.51	2.00E-09	4.39E-11	18.22
X^2	1.210152			0.999515			1.165294		

Table S2. Summary of the fitted values of branching factors introduced within a kinetic model defined in Eqs 3 as obtained by the target analysis of TA signals of the DMSO solutions of unimers and their complexes with Zn^{2+} ions.

parameter	PT	PT16
$arphi^f$	0.21	0.50
φ^{c}_{ISC}	0.77	0.74
$\varphi^{f}_{\rm ISC}$	0.77	0.98
$arphi_{ m T}$	1.0	0.15



Figure S1: The kinetic traces of the TA signal (in mOD) at the maxima of the respective bands (see the common legend and the main text: blue–GSB, green–SE, cyan–singlet ESA, magenta–triplet ESA). The red dashed lines show the fitted curves resulting from the global analysis using the sequential kinetic scheme. The fits show good overlap in all cases. Each panel shows kinetic traces of one material: (a) – unimer T, (b) – dynamer PT, (c) – unimer T16, (d) – dynamer PT16, (e) – unimer B23.



Figure S2. Transient absorption spectra (black crosses) of the solutions of unimer T (a), unimer T16 (b) and unimer B23 (c). Delay time 1 ps. Pump beam excitation centered at 438 nm (unimers T and T16) and 344 nm (unimer B23). Spectra decomposed into sum of individual Gaussian peaks (color curves) by a procedure described in the text. The band at 792 nm seen in the T and T16 spectra is an artifact caused by the spectrum of the probe beam.



Figure S3. Comparison of the normalized optical absorbance spectra of the studied solutions at low concentration $c = 3 \times 10^{-6}$ M (a) and high concentration $c = 10^{-4}$ M (b).



Figure S4. Comparison of the peak-value-normalized photoluminescence spectra of the studied solutions at low concentration $c = 3 \times 10^{-6}$ M (a) and at high concentration $c = 10^{-4}$ M (b).



Figure S5. UV/vis spectra of PB23 in DMSO as a function of the solution concentration.



Figure S6. Comparison of the TA spectra recorded at long delay times *t* (see the legend) in the solutions of the free unimers (a) **T** and (b) **T16** (full black lines) and their respective dynamers (a) **PT** and (b) **PT16** (red dashed curves). In the case of couple **T** – **PT**, they show strong similarity, but differences suggest some influence of Zn^{2+} ions in **PT**. They are almost identical in the case of couple **T16** – **PT16**.



Figure S7. Comparison of the TA signal evolutions in the solution of (a) dynamer **PT** and (b) dynamer **PT16** in the spectral region of the GSB (453 and 459 nm, in panels (a) and (b), respectively), recorded using two different pump fluencies (as indicated in the legends). The time traces completely overlap over entire time window.