Supplementary materials

"Monomeric and tetrameric forms of petroporphyrin VO-EtioP-III: Effect of solid-state aggregation on electronic absorption spectra"

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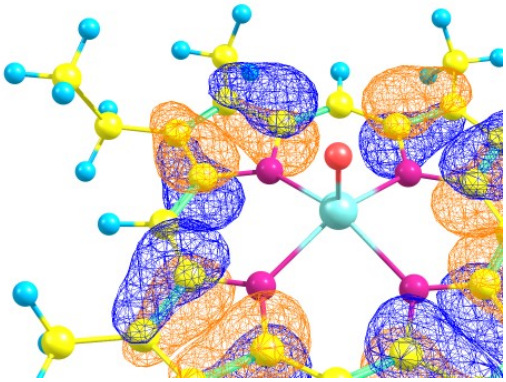
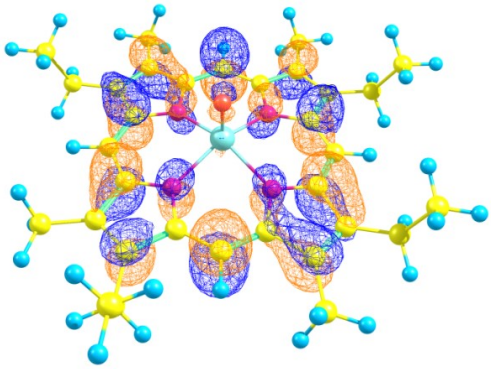
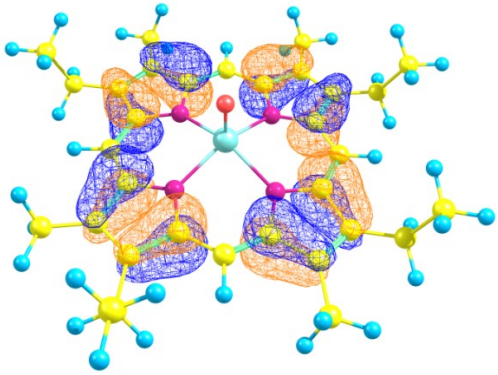
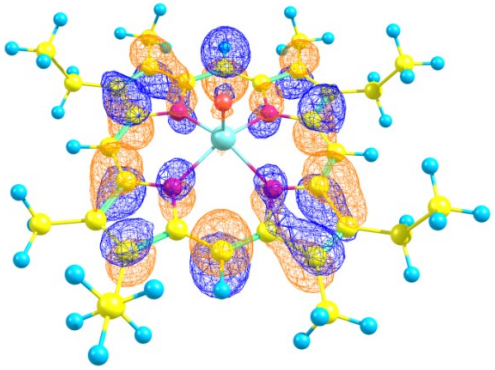
Table S1. Calculated composition of the lowest excited states and corresponding oscillator strengths along with the shapes of the orbitals participating in the electronic transitions for VO-EtioP-III.

λ, nm	F	%	Orbitals	
			From	To
607	0.02	32	 α-HOMO¶ (a)	 α-LUMO¶ (e)
		29	 β-HOMO¶ (a)	 β-LUMO¶ (e*)
		¶ Since monomeric VO-EtioP-III molecule is an open-shell system, the spectra were calculated using the sTDDFT approach, where two sets of orbitals α- and β- are optimized separately. Shapes of α-HOMO and β-HOMO (as well as LUMOs) have no visual differences, but there is some numeric inequality of the contributions of α-HOMO→α-LUMO and β-HOMO→β-LUMO transitions to the Q-band.		

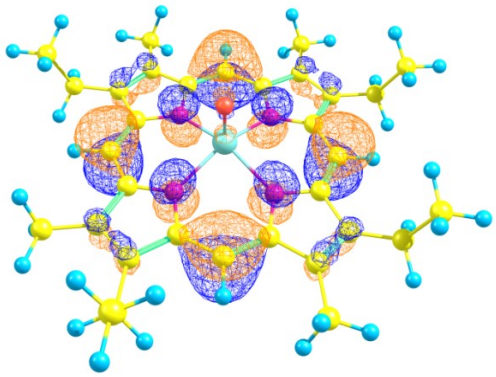
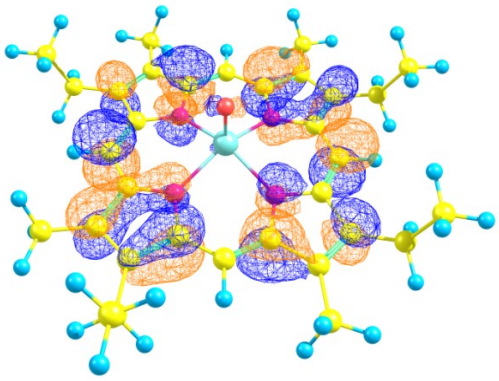
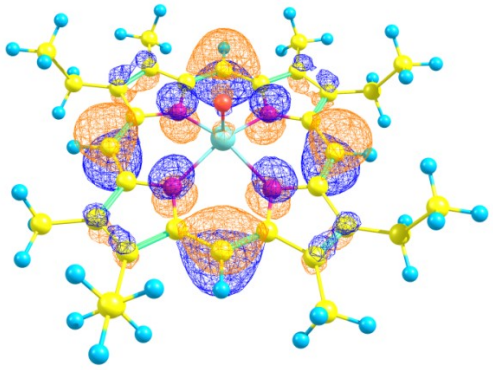
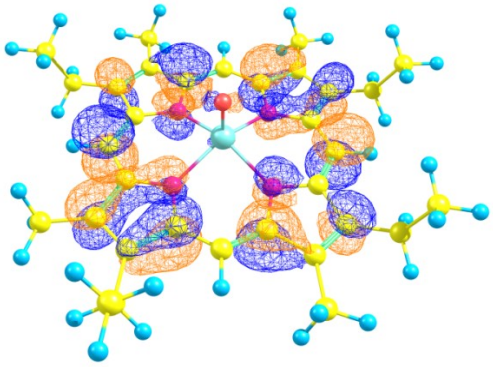
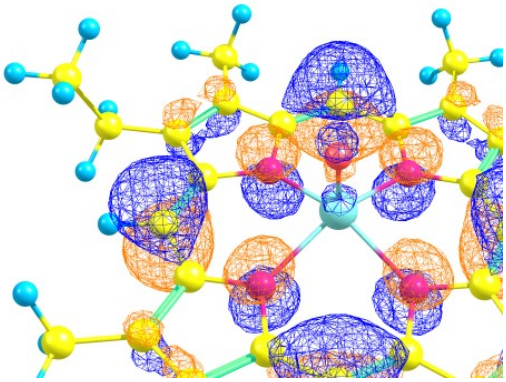
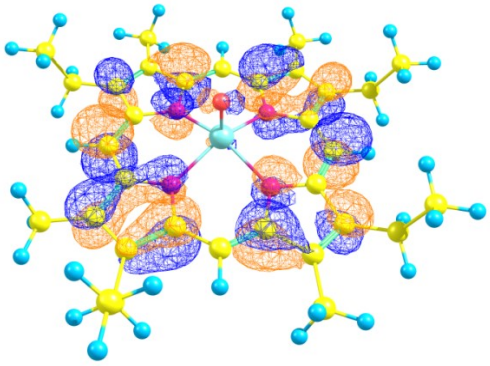
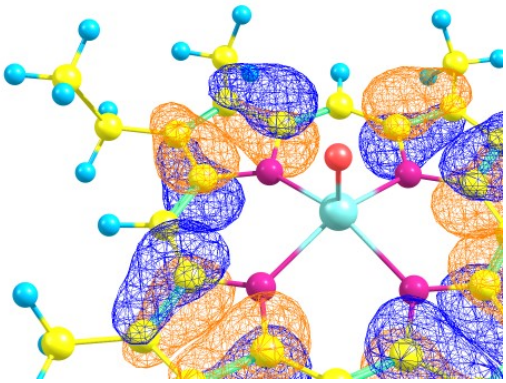
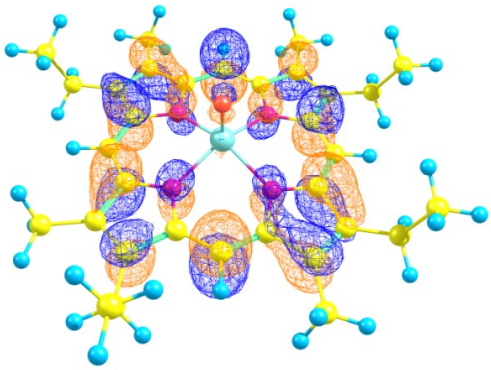
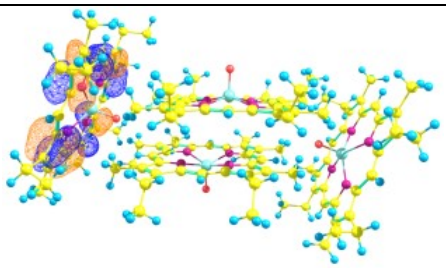
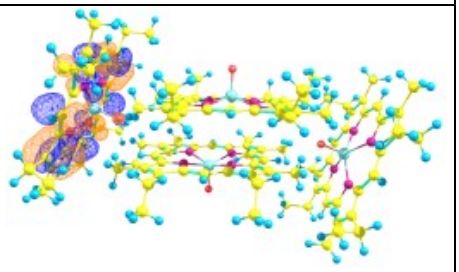
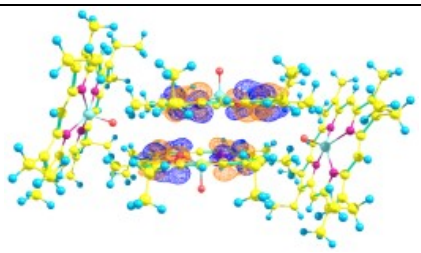
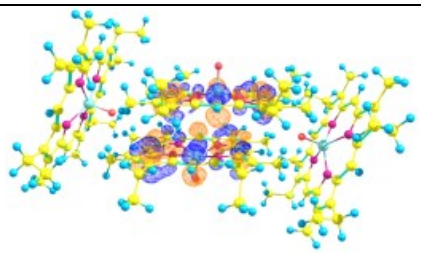
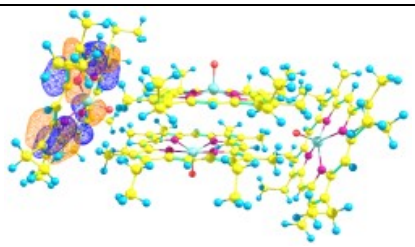
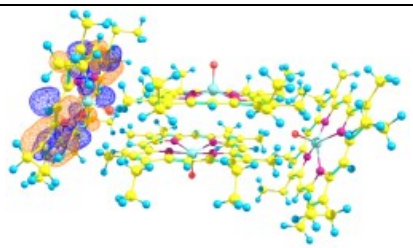
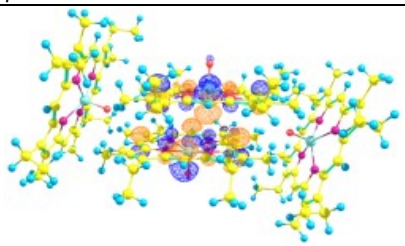
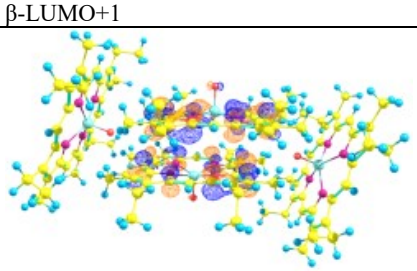
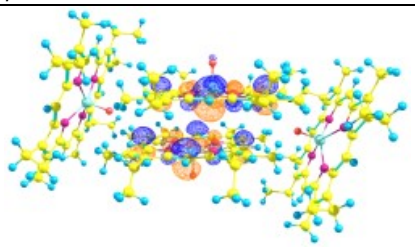
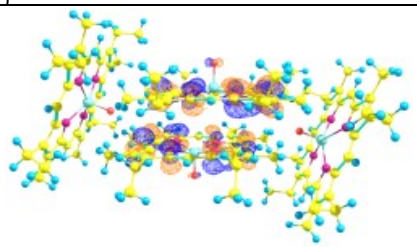
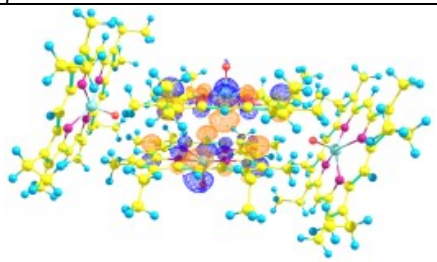
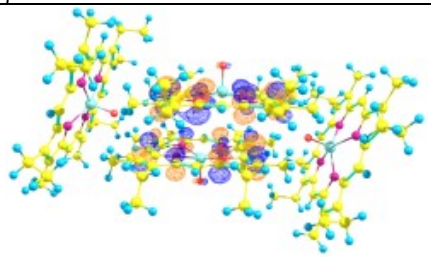
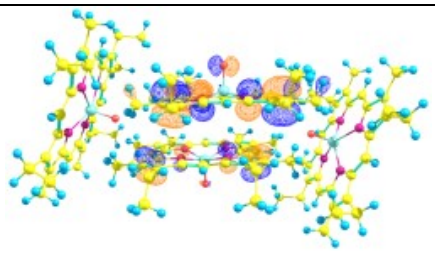
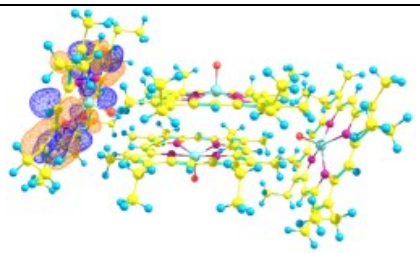
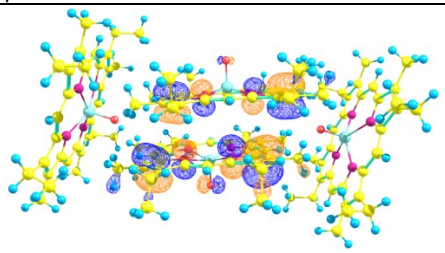
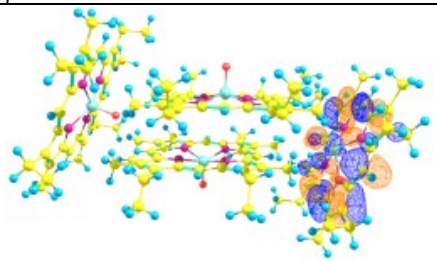
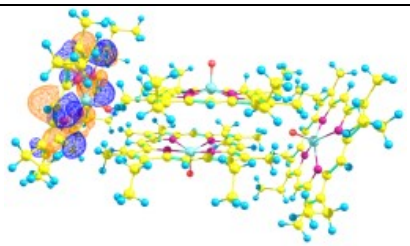
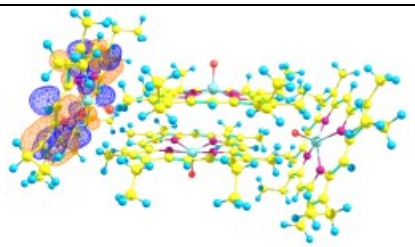
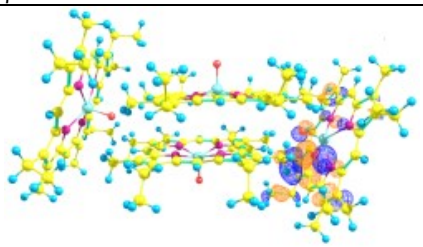
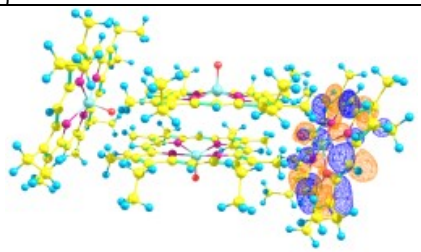
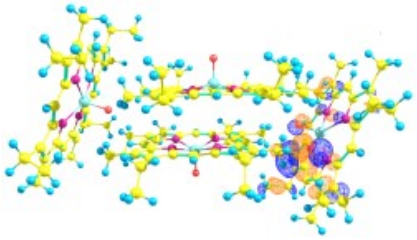
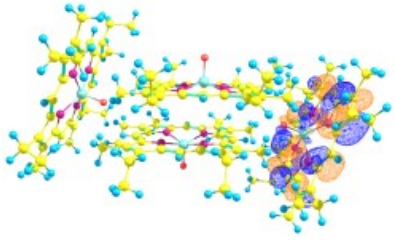
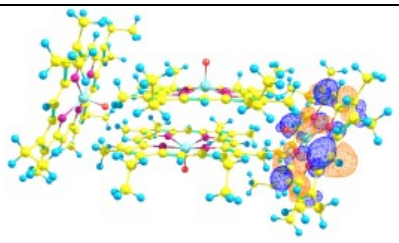
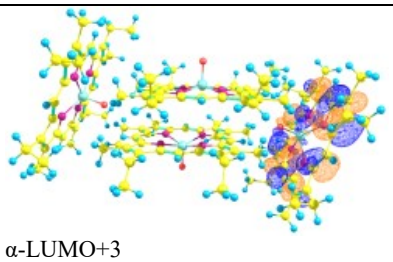
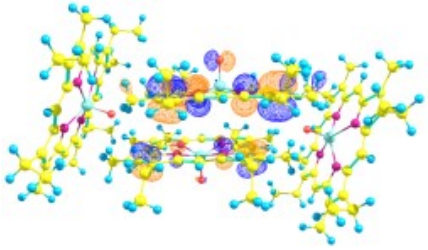
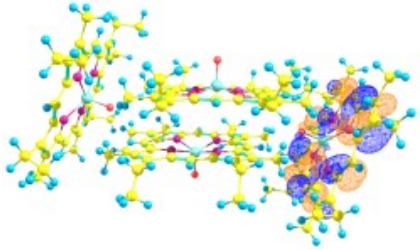
		20	 β-HOMO-1 (a)	 β-LUMO (e*)
381	1.03	18	 β-HOMO-1 (a)	 β-LUMO (e*)
		18	 α-HOMO-1 (a)	 α-LUMO (e*)
		11	 α-HOMO (a)	 α-LUMO (e*)

Table S2. Calculated composition of the lowest excited states, corresponding oscillator strengths, shapes of the orbitals participating in the electronic transitions in the VO-EtioP-III tetramer.

λ, nm	F	%	Orbitals	
			From	To
614	0.06	11	 α-HOMO-4	 α-LUMO+1
		10	 α-HOMO	 α-LUMO+5
		10	 β-HOMO-4	 β-LUMO+1
480	0.04	25	 β-HOMO-3	 β-LUMO+6
		25	 β-HOMO-2	 β-LUMO+7
		21	 α-HOMO-3	 α-LUMO+6

392	0.27	10	 β-HOMO-10	 β-LUMO+1
		10	 α-HOMO-10	 α-LUMO
		10	 β-HOMO-6	 β-LUMO+1
383	0.35	10	 α-HOMO-16	 α-LUMO
		8	 α-HOMO-16	 α-LUMO+3
		5	 α-HOMO-7	 α-LUMO+3
382	0.6	15	 β-HOMO-10	 β-LUMO+3

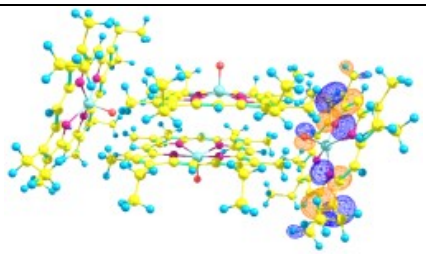
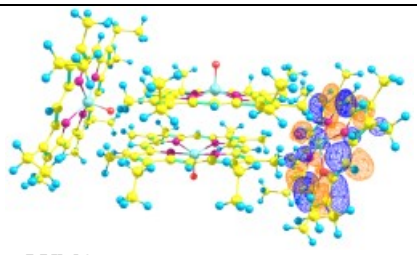
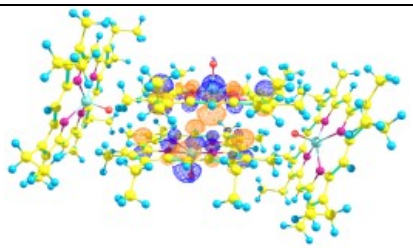
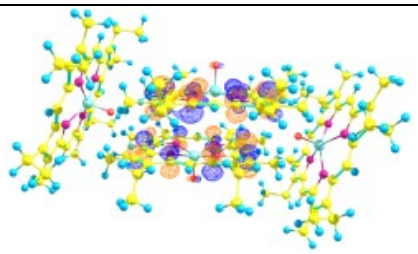
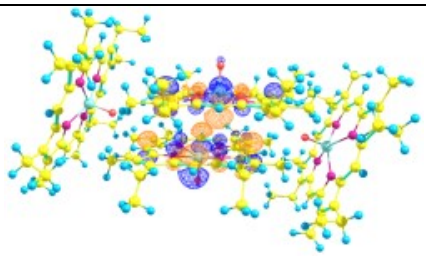
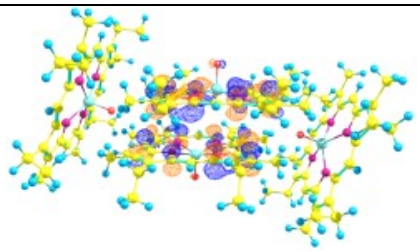
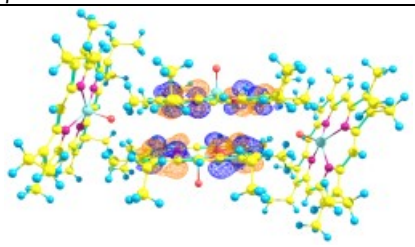
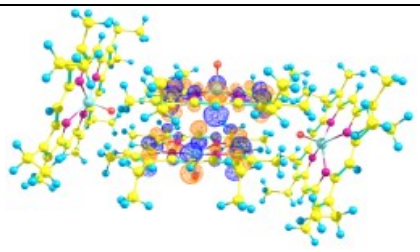
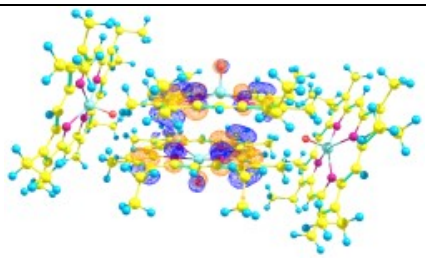
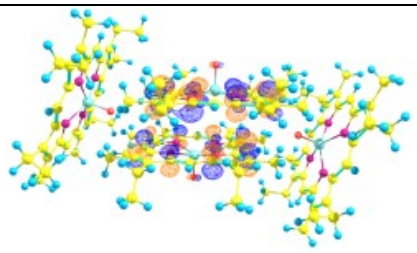
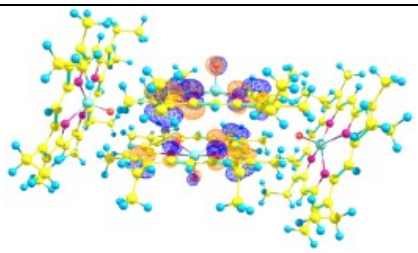
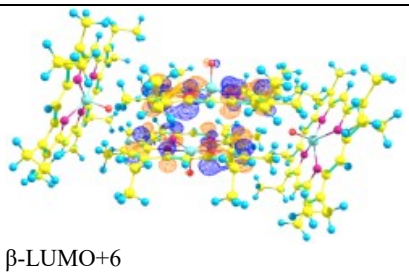
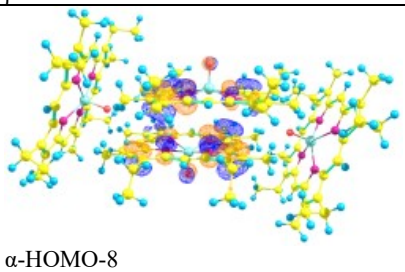
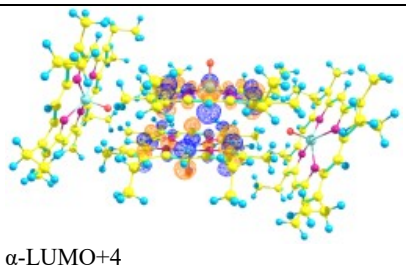
		7	 α-HOMO-19	 α-LUMO
366	1.00	10	 α-HOMO-3	 α-LUMO+6
		9	 β-HOMO-3	 β-LUMO+6
		6	 α-HOMO-1	 α-LUMO+4
359	0.65	7	 α-HOMO-8	 α-LUMO+6
		6	 β-HOMO-8	 β-LUMO+6
		5	 α-HOMO-8	 α-LUMO+4

Figure S1. Comparison of experimental spectra of VO-EtioP-III and InCl-EtioP-I in chloroform solutions (left panel) and thin films (right panel).

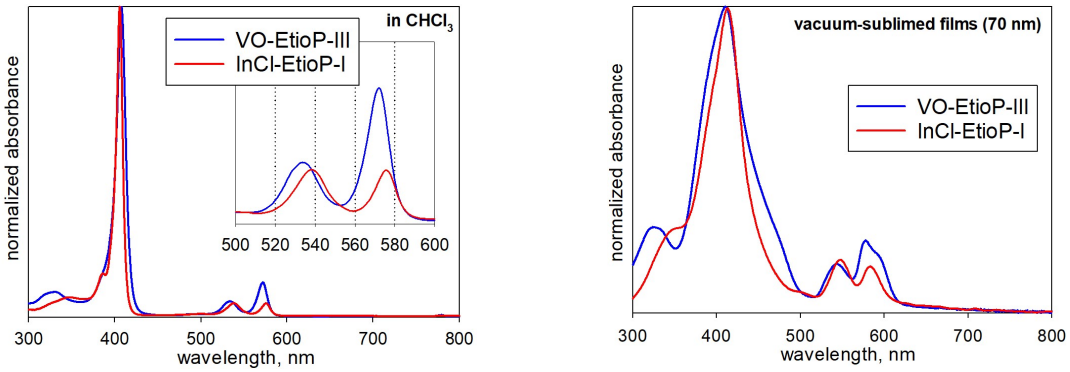
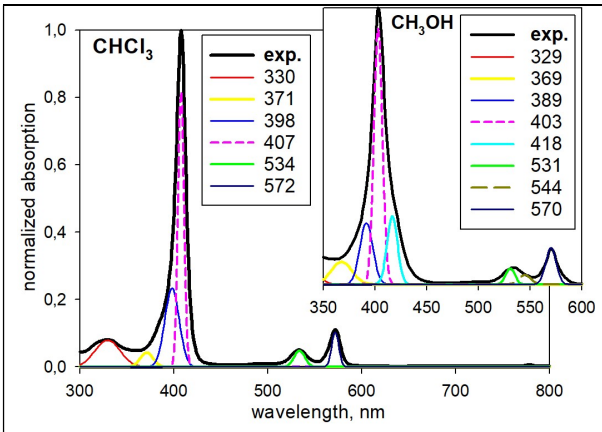
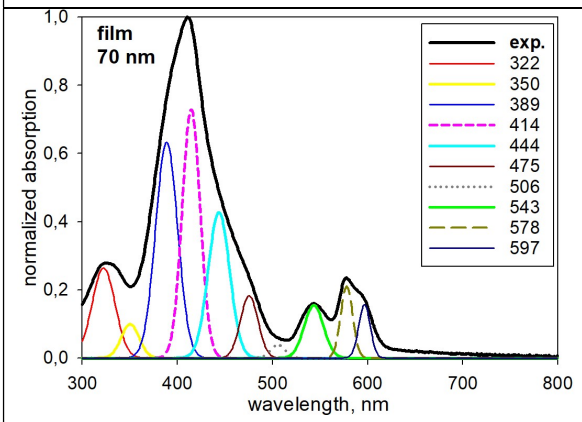


Figure S2.

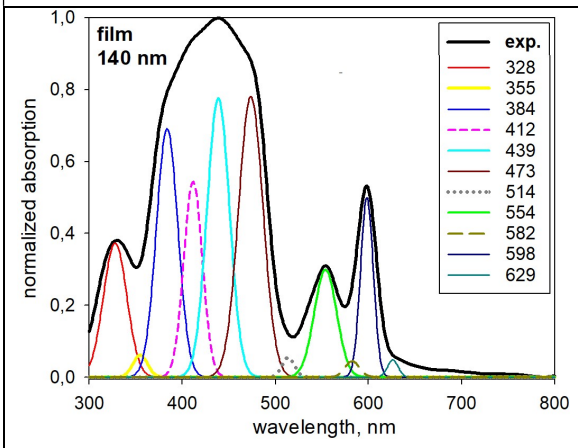


← Deconvolution of experimental spectrum of VO-EtioP-III in chloroform solution using a minimum number of Gaussian components [15]. The UV-band (λ_{max} = 329 nm) is not deconvoluted. The baseline is subtracted. The fitting error is less than 6%. **The inset** shows the deconvolution for a methanol solution where both Q- and Soret bands split into two components. This is caused by the solvent envelope and/or perhaps the strong tendency of VO-EtioP-III molecules to aggregate even in dilute alcohol solutions – see, [2].



← Deconvolution of experimental spectrum of a 70 nm thick vacuum-deposited film shown in **Figure 2**. The fitting error is less than 8%. The increase in the half-width of the subpeaks (solid-state broadening) was no more than 15-25%.

As seen from the Figure, bathochromic shift of the Q-band and Soret bands is accompanied by splitting and increase in intersubpeak distance, *i.e.* broadening.



← Similarly deconvoluted spectrum of a 140 nm thick VO-EtioP-III film deposited under identical conditions to a thinner film (taken from Ref. [2]).

The difference in the spectra of thinner and thicker film is due to an increase in the relative intensity of low-energy subpeaks (except that at ~580 nm), while their positions change very slightly. As a result, the Soret-band becomes broader.