

Probing the excited state dynamics of a new family of Cu(I)-complexes with an enhanced light absorption capacity: Excitation-wavelength dependent population of states through branching

Table S1. Time constants of the free ligands after excitation at 390nm in DCM.

	<i>p</i> -MeO-BIAN (1)	<i>p</i> -Me-BIAN (2)	<i>p</i> -Cl-BIAN (3)	<i>o</i> -Ph-BIAN (4)	<i>m</i> -Cl-BIAN (5)	<i>m</i> -CF ₃ -BIAN (6)
τ_1 (ps)	0.20	0.22	0.25	0.16	0.21	0.22
τ_2 (ps)	46	38	40	39	29	39

Table S2. Time constants of the Cu(I)-complexes after excitation at 390 nm in DCM.

	[Cu(1) ₂]BF ₄	[Cu(2) ₂]BF ₄	[Cu(3) ₂]BF ₄	[Cu(4) ₂]BF ₄	[Cu(5) ₂]BF ₄	[Cu(6) ₂]BF ₄
τ_1 (ps)	0.45	0.05	0.09	0.67	0.08	0.08
τ_2 (ps)	7.2	2.4	2.1	2.6	2.4	2.0
τ_3 (ps)	51	38	43	42	30	42

Table S3. Time constants of the Cu(I)-complexes in o-DCB after excitation at 390 nm.

	[Cu(1) ₂]BF ₄	[Cu(2) ₂]BF ₄	[Cu(3) ₂]BF ₄	[Cu(4) ₂]BF ₄	[Cu(5) ₂]BF ₄	[Cu(6) ₂]BF ₄
τ_1 (ps)	0.13	0.04	0.10	0.30	0.19	0.12
τ_2 (ps)	3.4	1.2	1.4	1.9	5.0	1.9
τ_3 (ps)	50	38	41	49	33	44

Table S4. Time constants of the Cu(I)-complexes after excitation at 780 nm in DCM.

	[Cu(1) ₂]BF ₄	[Cu(2) ₂]BF ₄	[Cu(3) ₂]BF ₄	[Cu(4) ₂]BF ₄	[Cu(5) ₂]BF ₄	[Cu(6) ₂]BF ₄
τ_1 (ps)	0.21	0.03	0.18	0.36	0.16	0.06
τ_2 (ps)	2.1	1.0	1.7	2.7	1.0	1.3
τ_3 (ps)	39	34	41	40	29	42

Table S5. Time constants of the Cu(I)-complexes after excitation at 780 nm in o-DCB.

	[Cu(1) ₂]BF ₄	[Cu(2) ₂]BF ₄	[Cu(3) ₂]BF ₄	[Cu(4) ₂]BF ₄	[Cu(5) ₂]BF ₄	[Cu(6) ₂]BF ₄
τ_1 (ps)	0.10	0.06	0.08	0.24	0.04	0.05
τ_2 (ps)	1.7	1.2	0.9	2.6	0.7	1.6
τ_3 (ps)	42	38	38	37	28	42

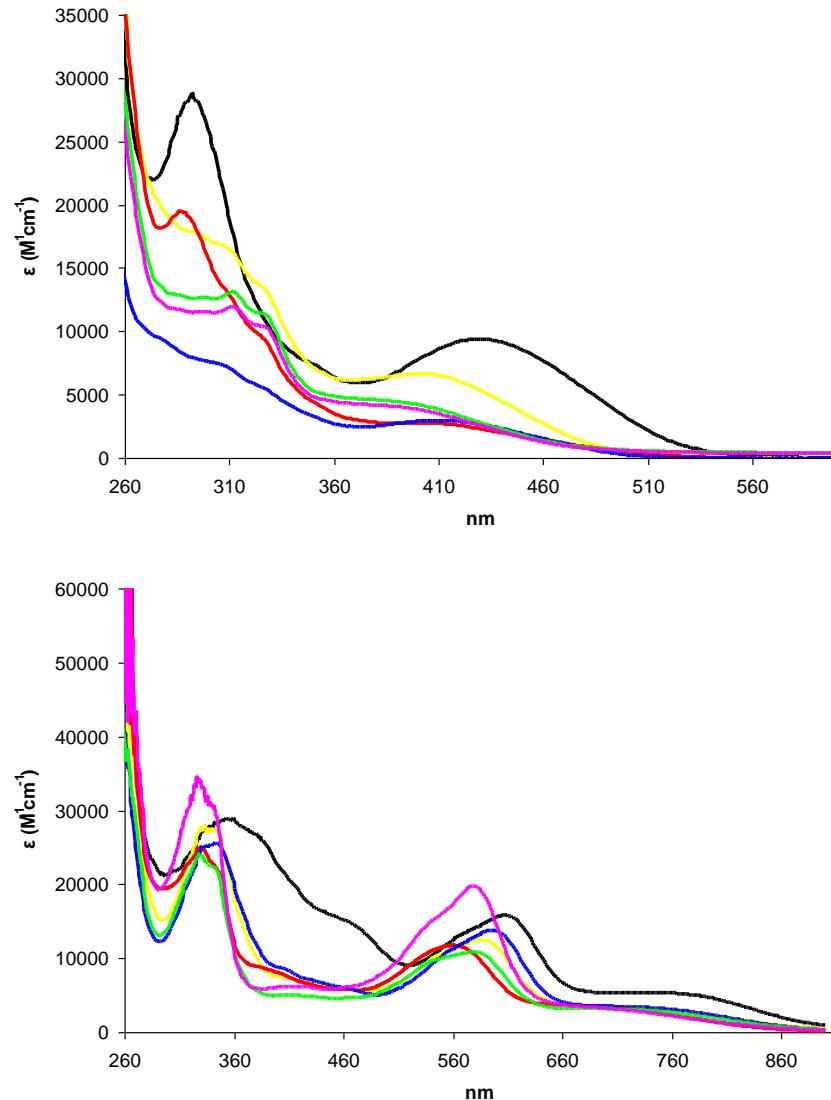


Fig S1. (top) : Absorption spectra of the ligands **1** (black), **2** (blue), **3** (yellow), **4** (red), **5** (green) and **6** (magenta) in DCM solution. (bottom) : Absorption spectra of the Cu(I)-complexes of **1** (black), **2** (blue), **3** (yellow), **4** (red), **5** (green) and **6** (magenta) in DCM solution.

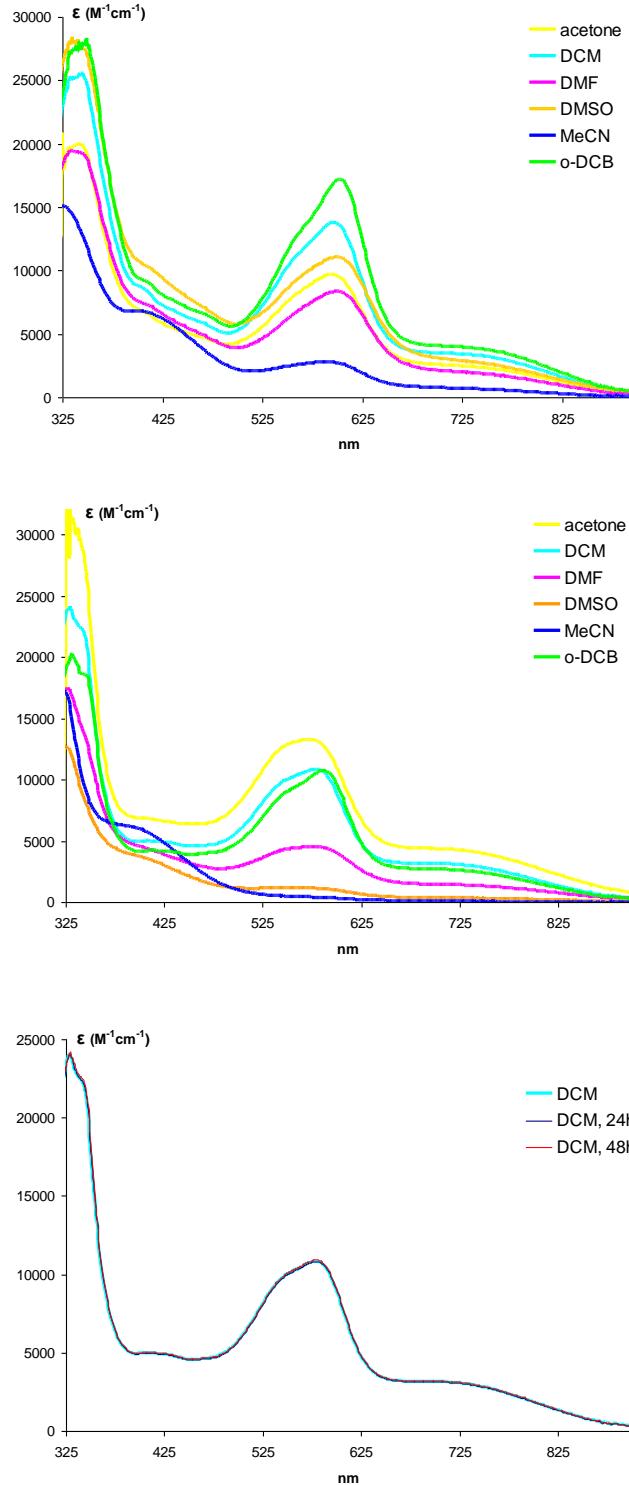


Fig S2. Ground state absorption spectra of $[\text{Cu(2)}_2]\text{BF}_4$ (top) and $[\text{Cu(5)}_2]\text{BF}_4$ (middle) recorded right after dissolution in a variety of solvents revealing the negligible effect of the polarity of the medium on position of the MLCT band. Except DCM and *o*-DCB, the complexes seem to decompose in other solvents tested after a few minutes as the intensity of the MLCT absorption gradually decreases and the solution changes its color towards yellow. The absorption spectra in the bottom reveal the thermal stability of $[\text{Cu(5)}_2]\text{BF}_4$ in DCM after 24 and 48 hours.

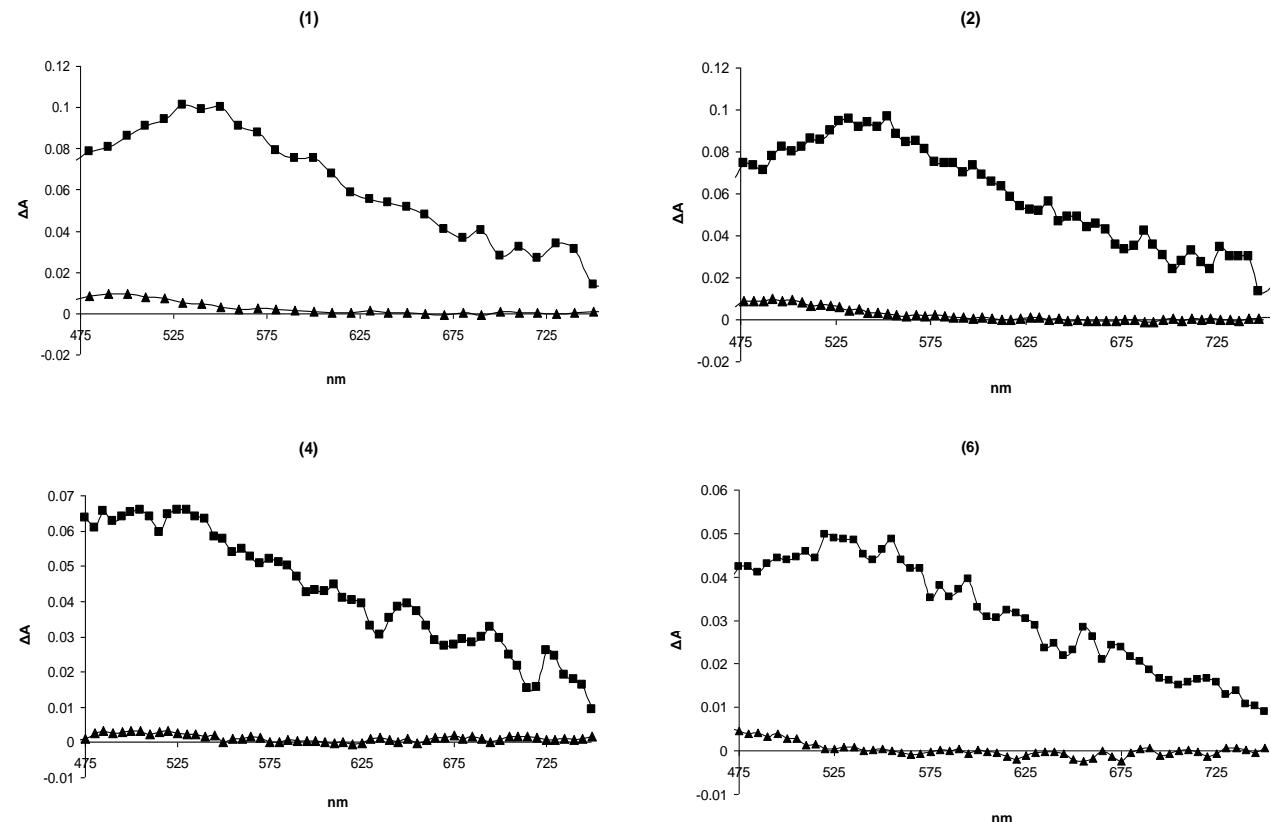


Fig S3. DAS of the ligands after 390 nm photoexcitation in DCM. The symbol (■) corresponds to the first time component and the (▲) to the second one (see Table S1). The number on the top of each plot is the ligands code according to Fig. 1.

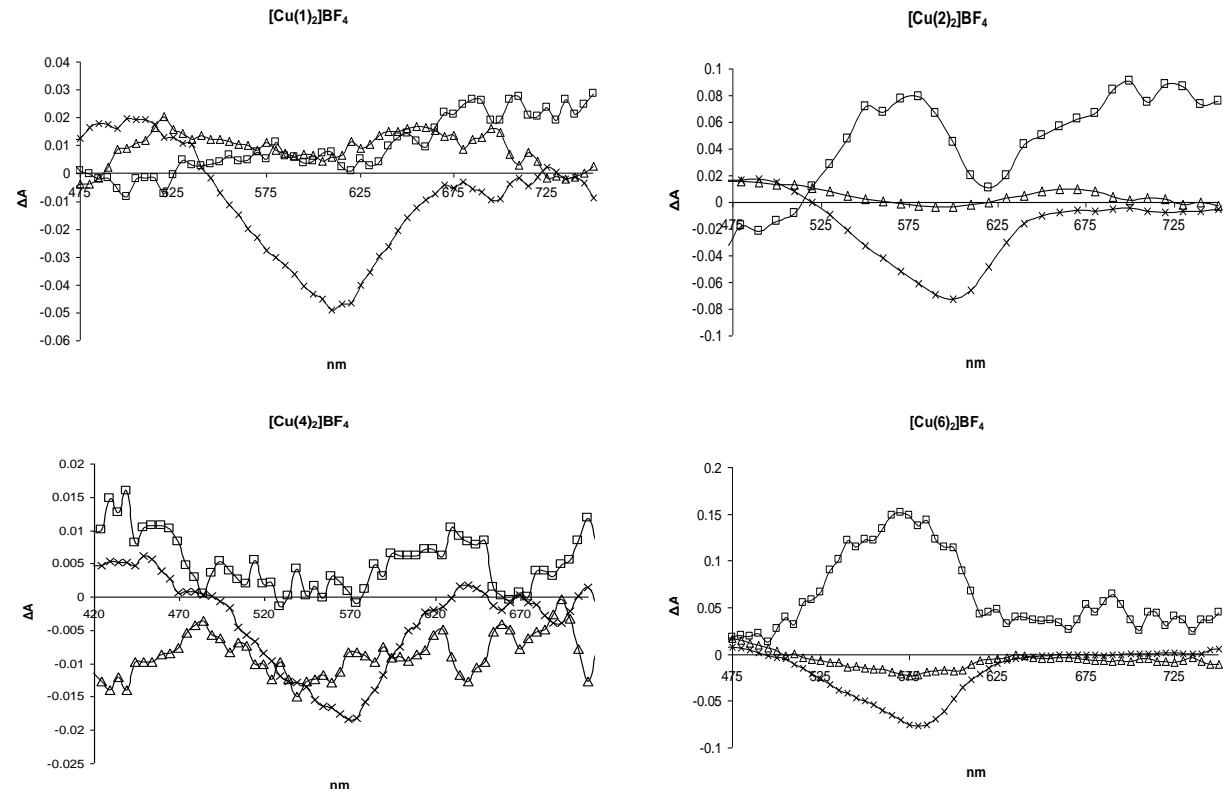


Fig S4. DAS of the complexes after 390 nm photoexcitation in DCM. The symbol (□) corresponds to the first time component, the (Δ) to the second and the (x) to the third time component (see Table S2).

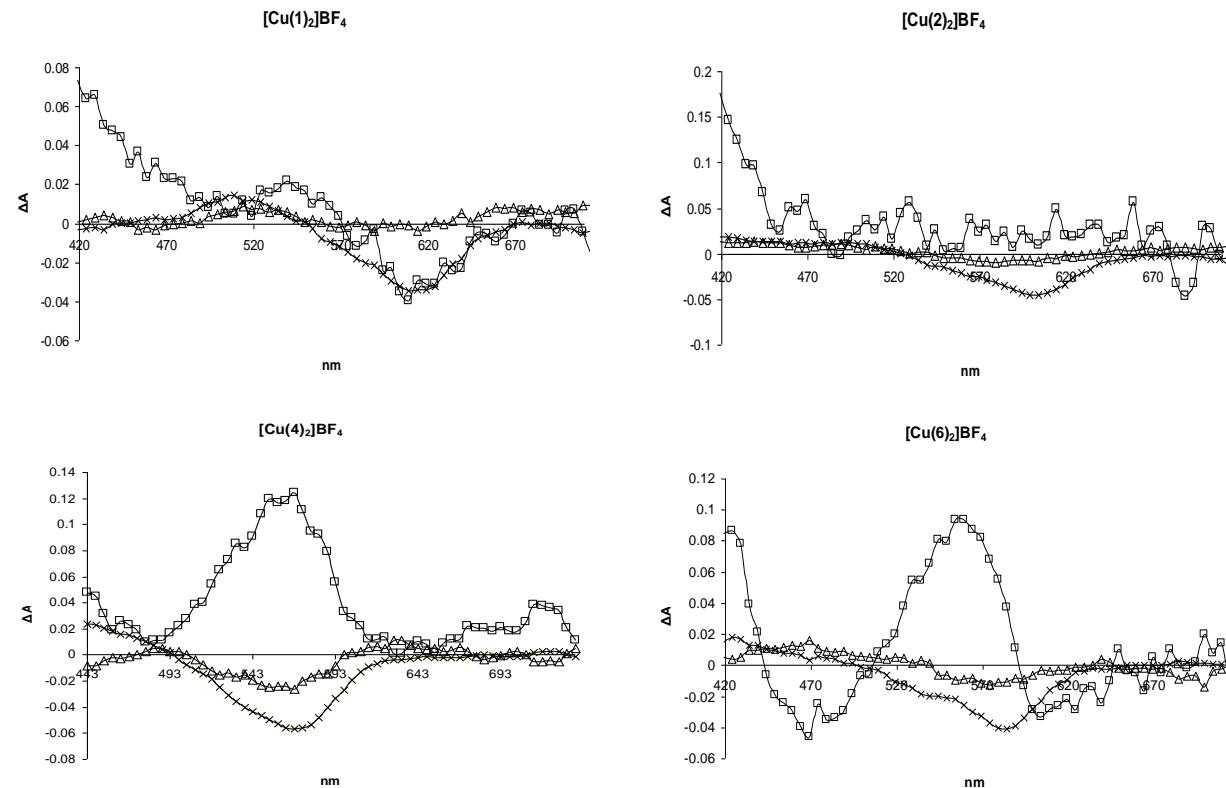


Fig S5. DAS of the complexes after 390 nm photoexcitation in o-DCB. The symbol (□) corresponds to the first time component, the (Δ) to the second and the (x) to the third time component (see Table S3).

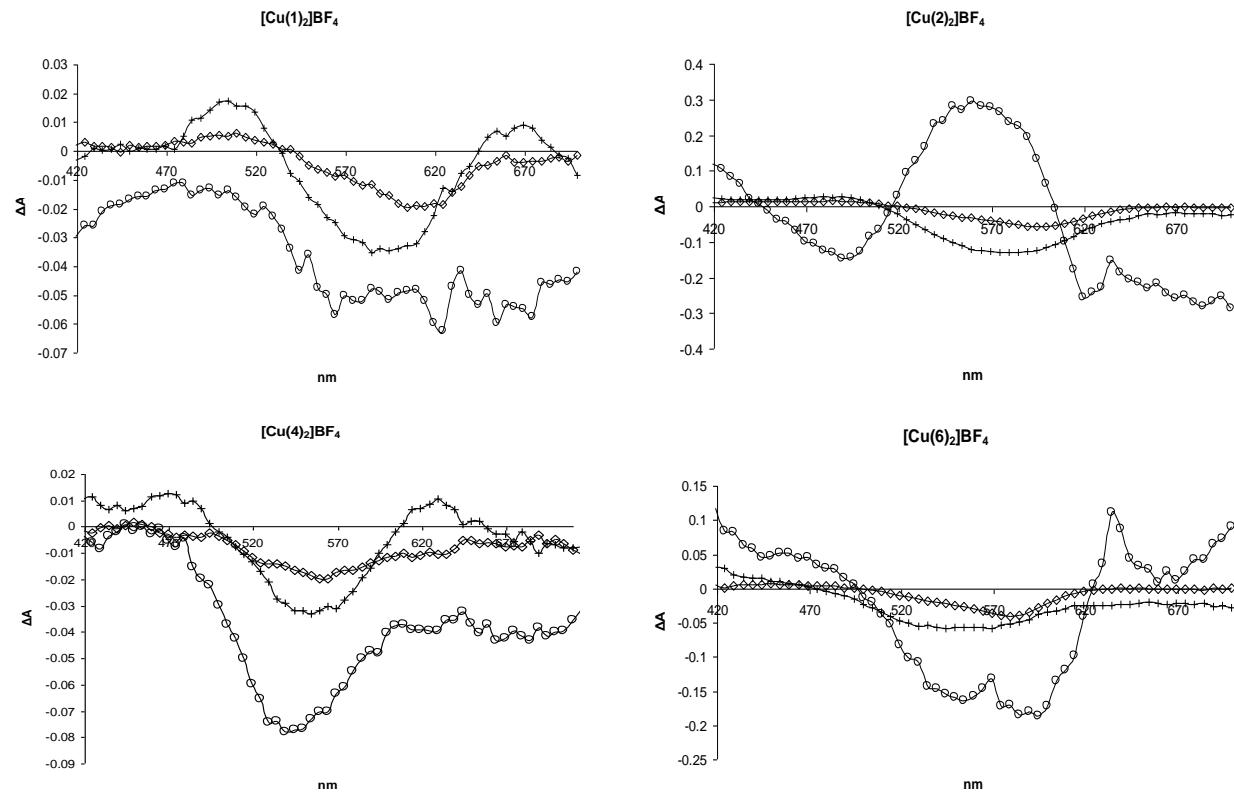


Fig S6. DAS of the complexes after 780 nm photoexcitation in DCM. The symbol (○) corresponds to the first time component, the (+) to the second and the (◊) to the third time component (see Table S4).

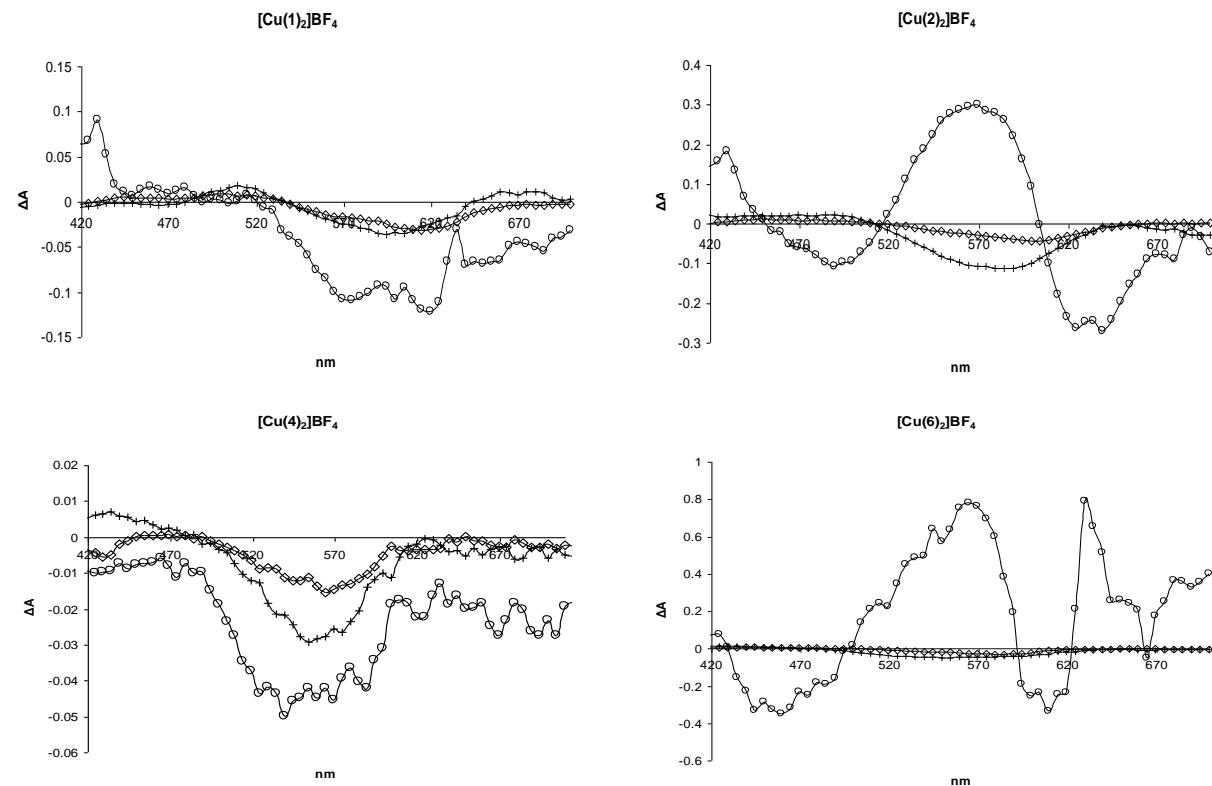


Fig S7. DAS of the complexes after 780 nm photoexcitation in o-DCB. The symbol (○) corresponds to the first time component, the (+) to the second and the (◊) to the third time component (see Table S5).