Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Synthesis, Electrochemical and Photophysical Studies of the Borondifluoride Complex of a meta-Linked Biscurcuminoid

Morgane Rivoal, Elena Zaborova, Gabriel Canard, Anthony D'Aléo,* Frédéric Fages

Aix Marseille Université, CNRS, CINaM UMR 7325, Campus de Luminy, Case 913, 13288 Marseille (France)

E-mail : daleo@cinam.univ-mrs.fr

Supporting information

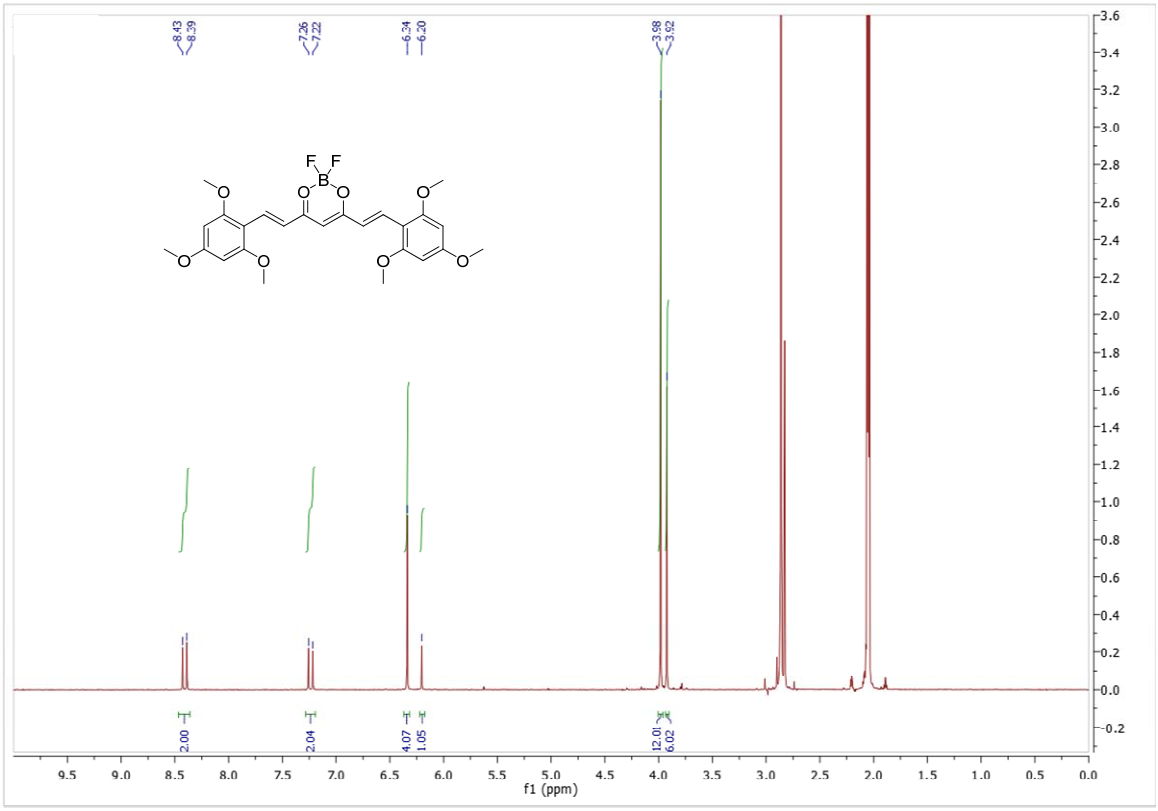

Figure NMR1. ^{1}H NMR spectrum of **1** ((1E,4Z,6E)-5-(difluoroboryloxy)-1,7-bis(2,4,6-trimethoxyphenyl)hepta-1,4,6-trien-3-one) in $(CD_3)_2CO$.

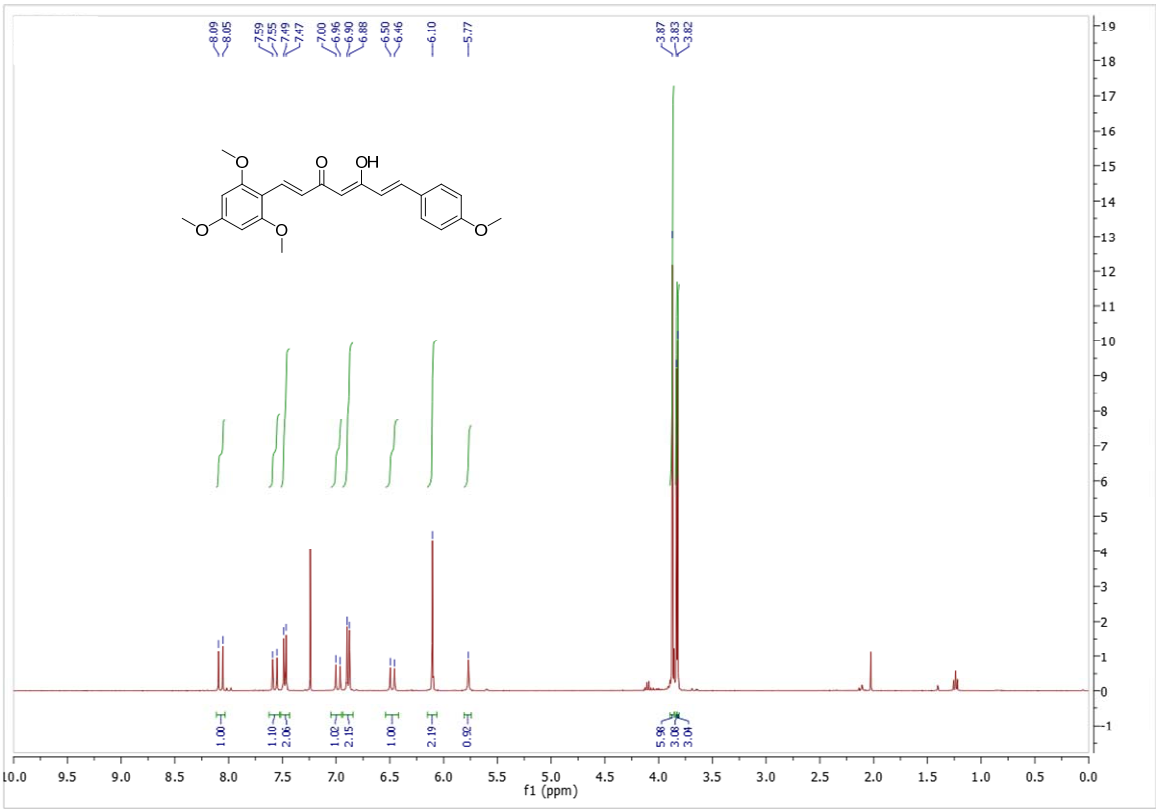

Figure NMR2. ^{1}H NMR spectrum of **Lig 3** ((1E,4Z,6E)-5-hydroxy-7-(4-methoxyphenyl)-1-(2,4,6-trimethoxyphenyl)hepta-1,4,6-trien-3-one) in $CDCl_3$.

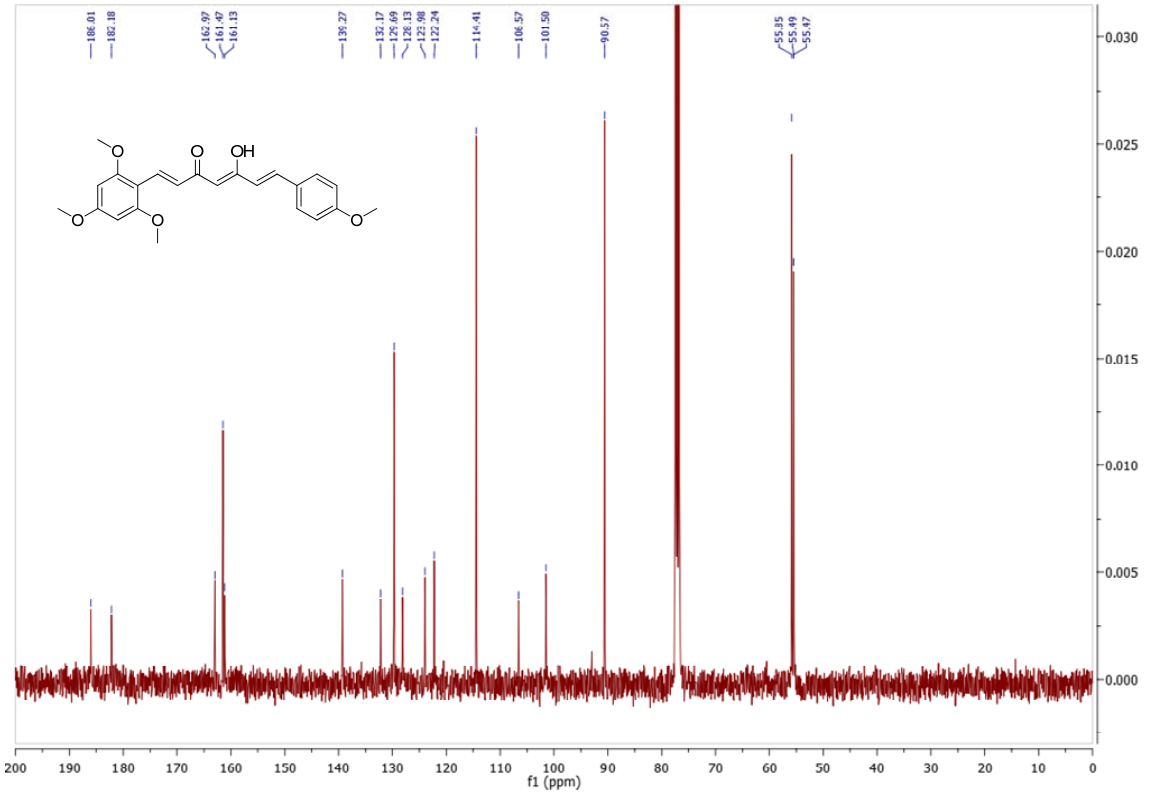

Figure NMR3. ^{13}C NMR spectrum of **Lig 3** ((1E,4Z,6E)-5-hydroxy-7-(4-methoxyphenyl)-1-(2,4,6-trimethoxyphenyl)hepta-1,4,6-trien-3-one) in $CDCl_3$.

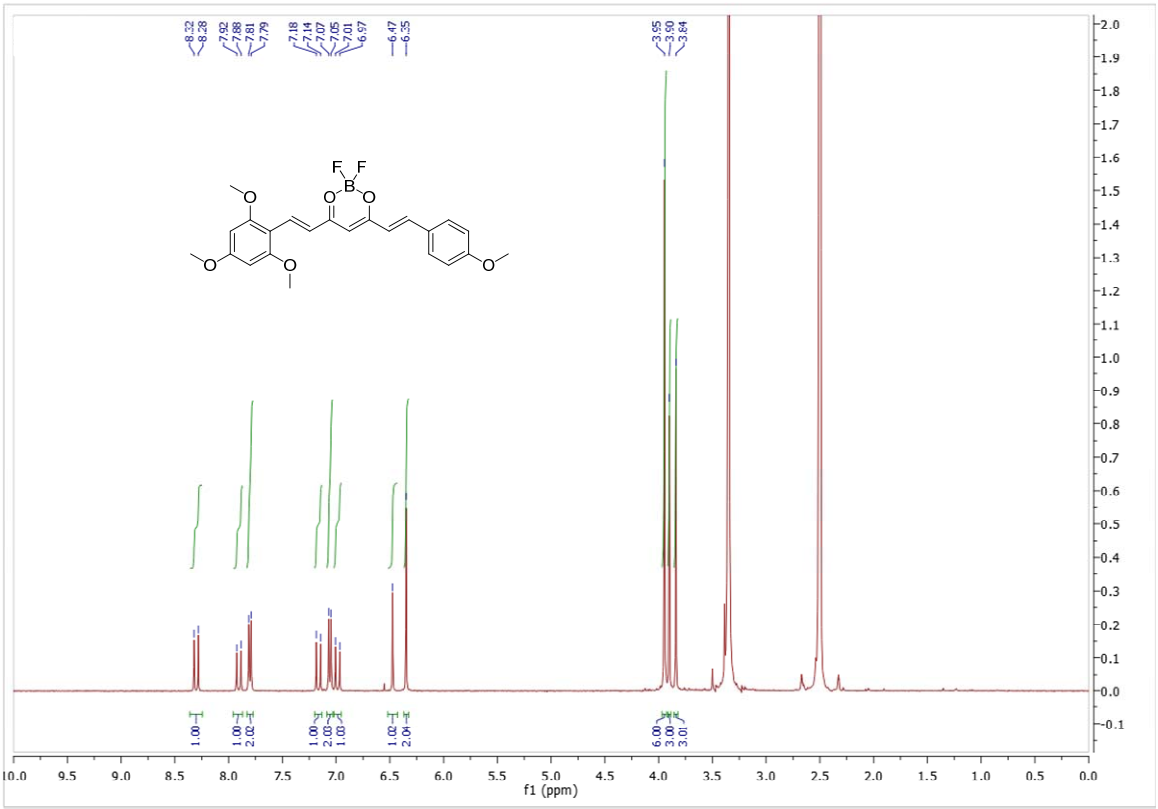

Figure NMR4. ^{1}H NMR spectrum of **3** ((1E,4Z,6E)-5-(difluoroboryloxy)-7-(4-methoxyphenyl)-1-(2,4,6-trimethoxyphenyl)hepta-1,4,6-trien-3-one) in DMSO-d_6.

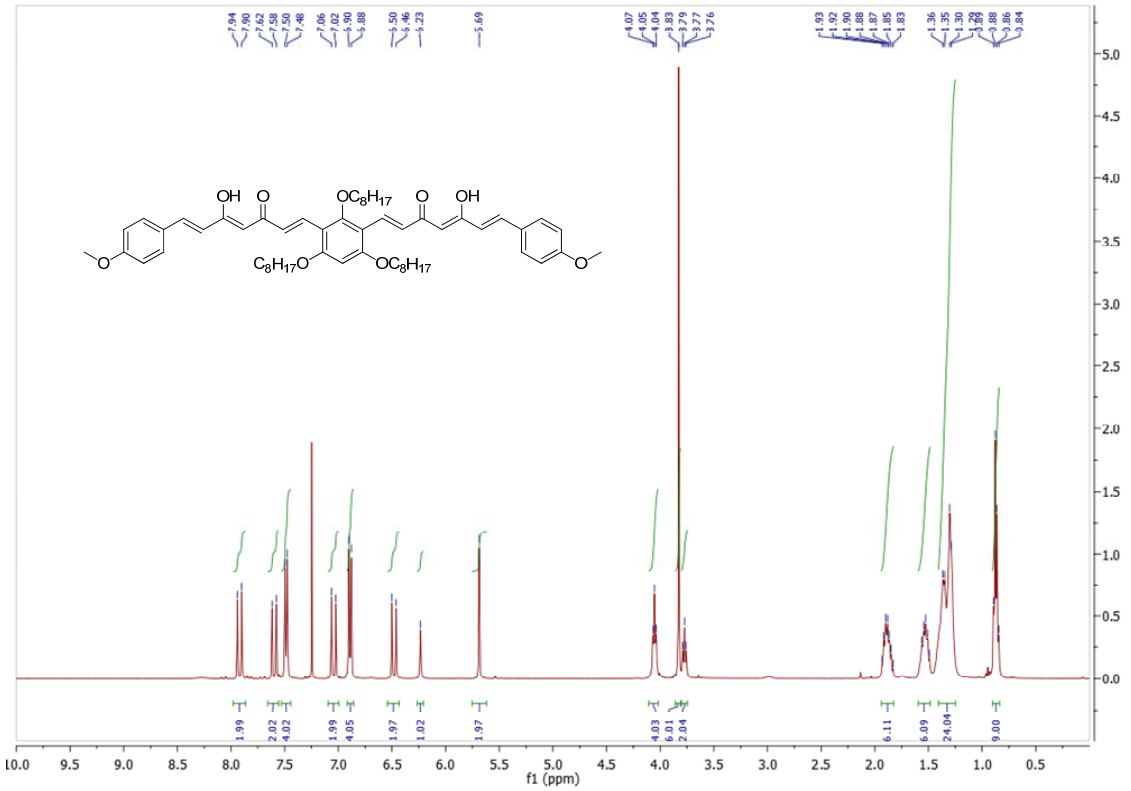

Figure NMR5. ^{1}H NMR spectrum of **Lig 4** ((1E,1'E,4Z,4'Z,6E,6'E)-1,1'-(2,4,6-tris(octyloxy)-1,3-phenylene)bis(5-hydroxy-7-(4-methoxyphenyl)hepta-1,4,6-trien-3-one)) in $CDCl_3$.

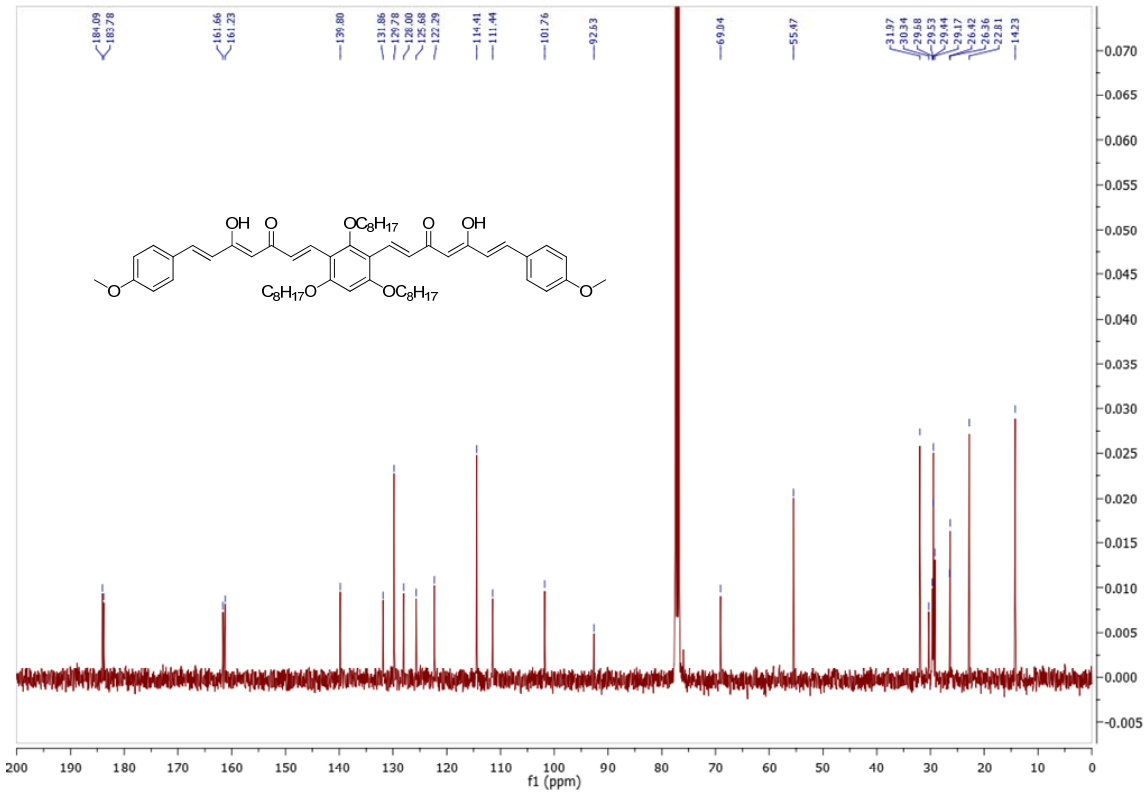

Figure NMR6. ^{13}C NMR spectrum of **Lig 4** ((1E,1'E,4Z,4'Z,6E,6'E)-1,1'-(2,4,6-tris(octyloxy)-1,3-phenylene)bis(5-hydroxy-7-(4-methoxyphenyl)hepta-1,4,6-trien-3-one)) in $CDCl_3$.

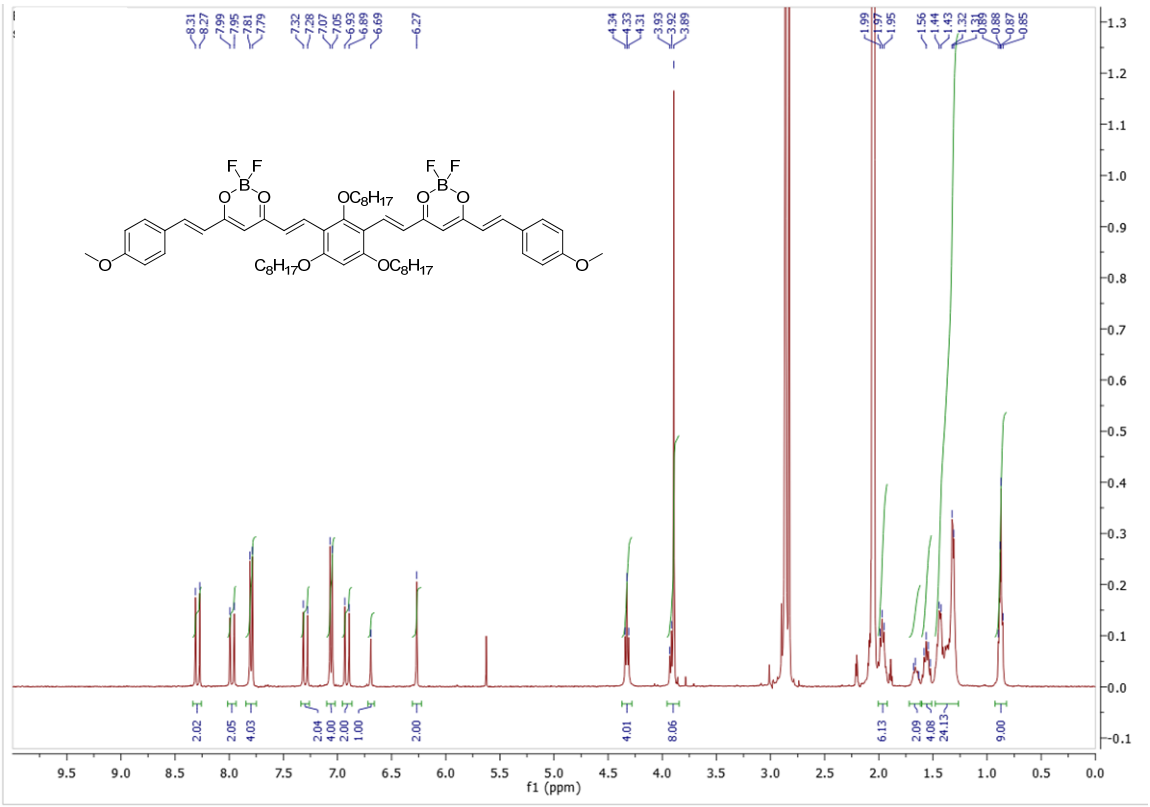

Figure NMR7. ^{1}H NMR spectrum of **4** ((1E,1'E,4Z,4'Z,6E,6'E)-1,1'-(2,4,6-tris(octyloxy)-1,3-phenylene)bis(5-(difluoroboryloxy)-7-(4-methoxyphenyl)hepta-1,4,6-trien-3-one)) in $(CD_3)_2CO$.

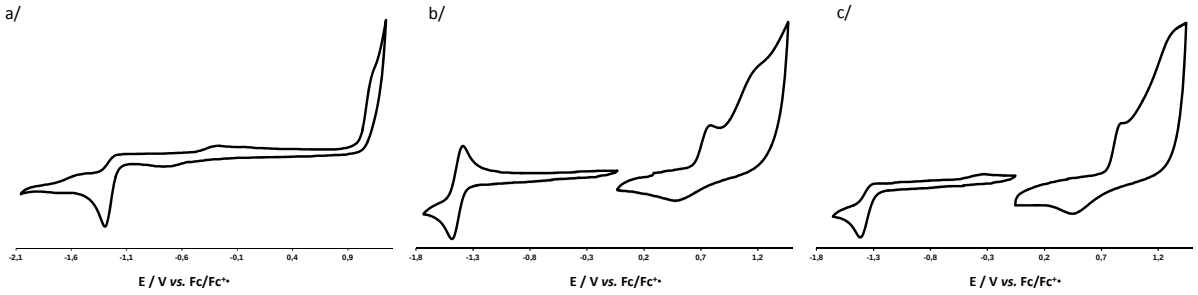

Figure S1. Cyclic voltammogram of the bis borondifluoride complex **1** (a), **2** (b) and **3** (c) in DCM solution containing 0.1M [(^{n}Bu$_4$N)PF$_6$] (Scan rate of 100 mV/s).

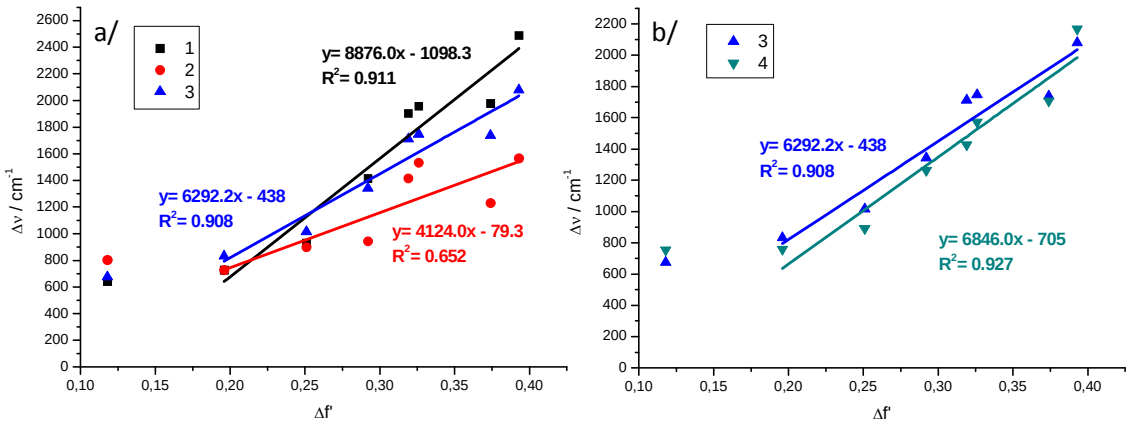

Figure S2. Lippert-Mataga plots for a/ **1** (■), **2** (●) and **3** (▲); b: **3** (▲) and **4** (▼) where Δf' = $[(\varepsilon - 1)/(2\varepsilon + 1)] - 0.5\,[(n^2 - 1)(2n^2 + 1)]$.

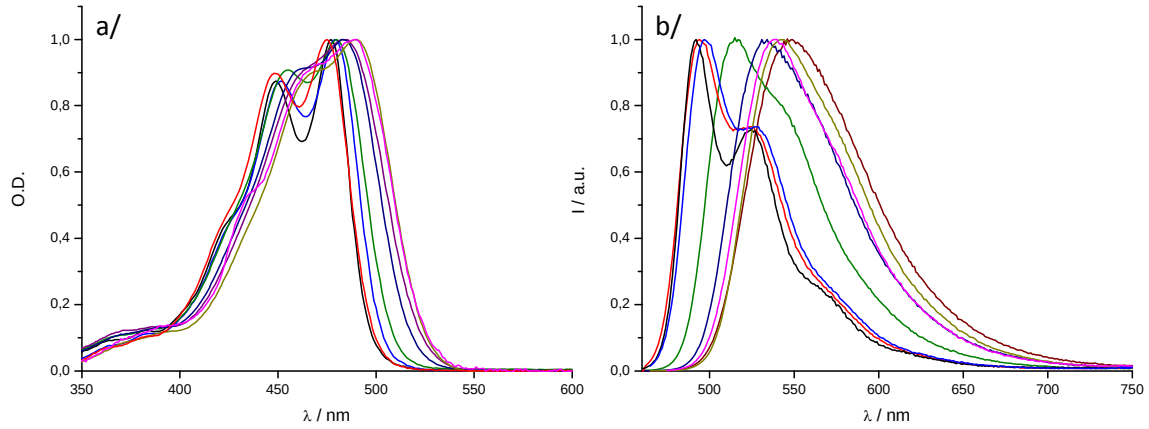

Figure S3. Electronic absorption (a) and fluorescence emission (b) spectra of compound **1** in solvents of different polarity at room temperature (λ_{exc} = 450nm; carbon tetrachloride (▬), n-dibutylether (▬), ethylic ether (▬), ethyl acetate (▬), dichloromethane (▬), 1,2-dichloroethane (▬), acetone (▬) and acetonitrile (▬)).

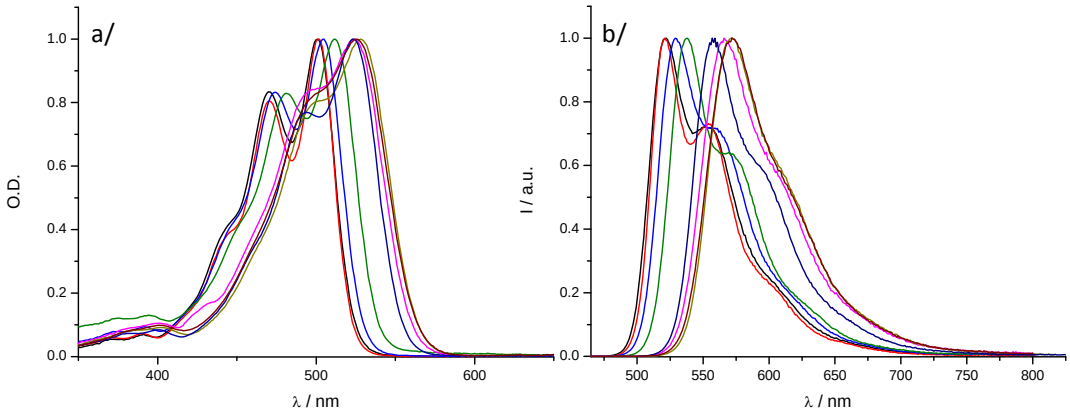

Figure S4. Electronic absorption (a) and fluorescence emission (b) spectra of compound **2** in solvents of different polarity at room temperature (λ_{exc} = 480nm; carbon tetrachloride (▬), n-dibutylether (▬), ethylic ether (▬), ethyl acetate (▬), dichloromethane (▬), 1,2-dichloroethane (▬), acetone (▬) and acetonitrile (▬)).

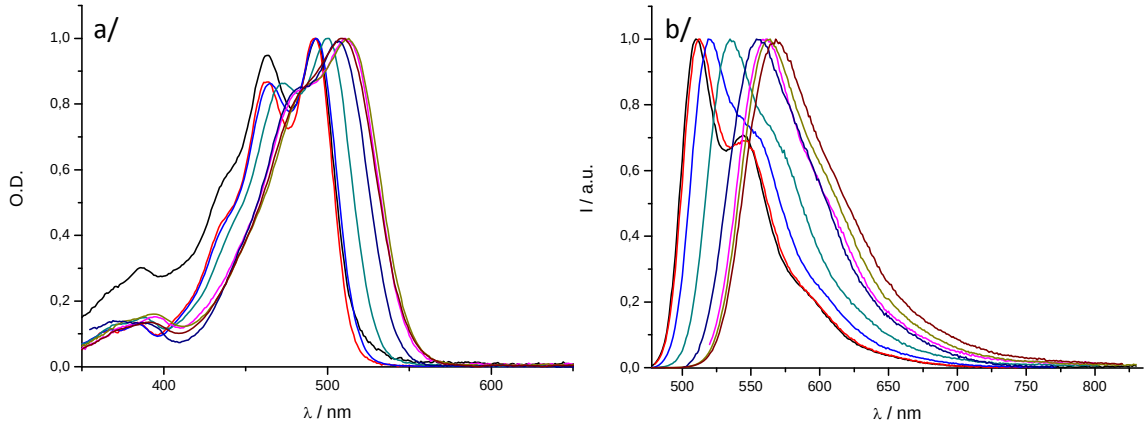

Figure S5. Electronic absorption (a) and fluorescence emission (b) spectra of compound **3** in solvents of different polarity at room temperature (λ_{exc} = 480nm; carbon tetrachloride (▬), n-dibutylether (▬), ethylic ether (▬), ethyl acetate (▬), dichloromethane (▬), 1,2-dichloroethane (▬), acetone (▬) and acetonitrile (▬)).

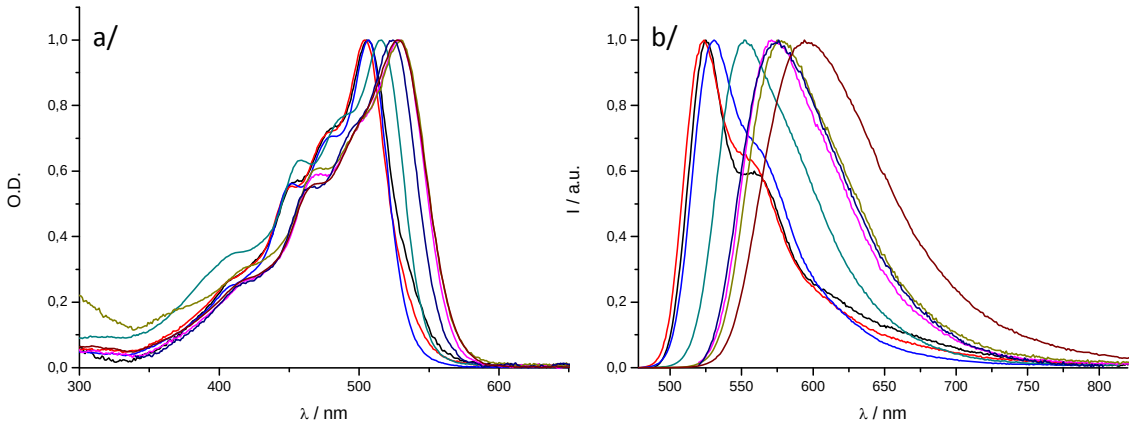

Figure S6. Electronic absorption (a) and fluorescence emission (b) spectra of compound **4** in solvents of different polarity at room temperature (λ_{exc} = 480nm; carbon tetrachloride (▬), n-dibutylether (▬), ethylic ether (▬), ethyl acetate (▬), dichloromethane (▬), 1,2-dichloroethane (▬), acetone (▬) and acetonitrile (▬)).

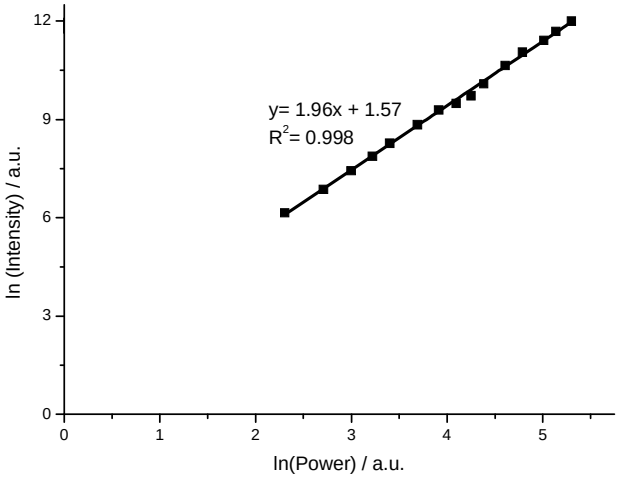

Figure S7. Dependencies of the fluorescence intensity versus laser excitation power for **1** (■, black) in DCM.

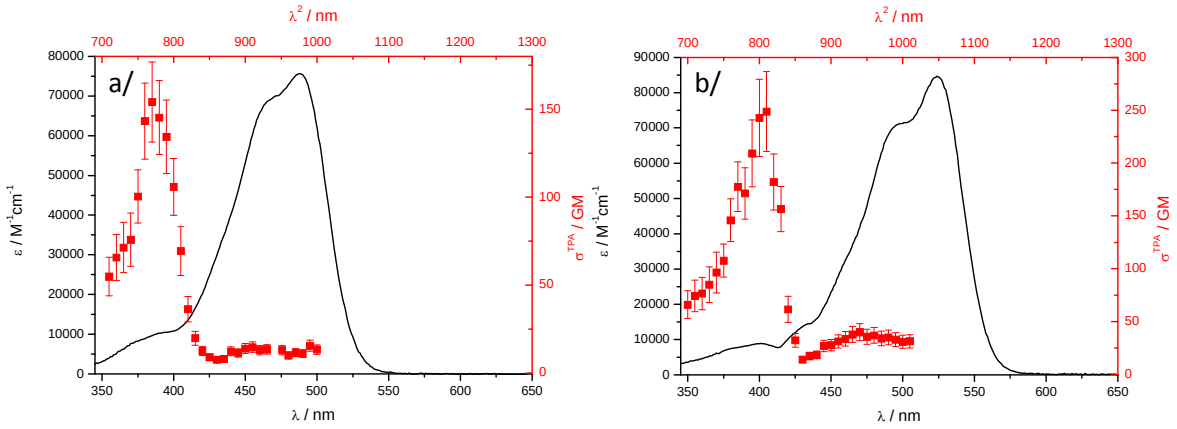

Figure S8. Two-photon excitation (▪ , higher x-coordinate and —, right y-coordinate) with their error bars, OPA spectra (—, lower x-coordinate and —, left y-coordinate) in DCM: a/ dye **1** and b/ dye **2**.

Table S1. Spectroscopic data and photophysical properties of compounds **1** and **2** in solvents of different polarity at room temperature[a]

	1							**2**						
solvent	λ_{abs}	λ_{em}	$\Delta\nu_{ST}$	Φ_f	τ_f	k_f	k_{nr}	λ_{abs}	λ_{em}	$\Delta\nu_{ST}$	Φ_f	τ_f	k_f	k_{nr}
CCl_4	477	492	639	0.20	0.50	4.0	16	501	522	803	0.27	1.03	2.6	7.1
Bu_2O	475	492	727	0.22	0.60	3.7	13	502	521	726	0.31	1.07	2.9	6.5
Et_2O	475	497	930	0.24	0.70	3.5	11	505	529	898	0.37	1.4	2.7	4.5
AcOEt	480	515	1415	0.35	0.88	3.9	7.4	512	538	944	0.45	1.6	2.8	3.4
DCM	488	538	1905	0.44	1.30	3.4	4.3	524	566	1416	0.52	1.72	3.0	2.8
DCE	490	542	1977	0.44	1.55	2.8	3.6	525	571	1534	0.53	1.75	3.0	2.7
Acetone	483	534	1980	0.45	1.49	3.0	3.7	523	559	1231	0.56	1.8	3.1	2.4
ACN	483	549	2490	0.51	1.55	3.3	3.2	525	572	1565	0.59	1.89	3.1	2.2

[a] Absorption maximum wavelengths λ_{abs} (nm). fluorescence maximum wavelengths λ_{em} (nm). Stokes shifts $\Delta\nu_{ST}$ (cm^{-1}). fluorescence quantum yields Φ_f. fluorescence lifetimes τ_f (ns). radiative k_f (10^8 s^{-1}) and nonradiative $k_{nr} = (1 - \Phi_f)/\tau_f$ (10^8 s^{-1}) rate constants; Bu_2O: n-dibutylether. Et_2O: ethylic ether. AcOEt: ethyl acetate. DCM: dichloromethane. DCE: 1.2-dichloroethane. ACN: acetonitrile.

Table S2. Spectroscopic data and photophysical properties of compounds **3** and **4** in solvents of different polarity at room temperature[a]

	3							**4**						
solvent	λ_{abs}	λ_{em}	$\Delta\nu_{ST}$	Φ_f	τ_f	k_f	k_{nr}	λ_{abs}	λ_{em}	$\Delta\nu_{ST}$	Φ_f	τ_f	k_f	k_{nr}
CCl_4	493	510	676	0.17	0.8	2.1	10	505	525	754	0.34	1.06	3.2	6.2
Bu_2O	492	513	832	0.22	0.95	2.3	8.2	504	524	757	0.36	1.13	3.2	5.6
Et_2O	493	519	1016	0.29	1.08	2.7	6.6	507	531	891	0.46	1.21	3.8	4.4
AcOEt	500	536	1343	0.37	1.59	2.3	3.9	516	552	1264	0.66	1.66	4.0	2.0
DCM	511	560	1712	0.46	1.74	2.6	3.1	528	571	1426	0.61	1.69	3.6	2.3
DCE	513	563.5	1747	0.48	1.75	2.7	3.0	529	577	1573	0.55	1.72	3.2	2.6
Acetone	507	556	1738.3	0.47	1.7	2.8	3.1	524	575.5	1708	0.21	1	2.1	7.9
ACN	508	568	2079.4	0.47	1.62	2.9	3.3	527	595	2169	0.12	<0.8	-	-

[a] Absorption maximum wavelengths λ_{abs} (nm). fluorescence maximum wavelengths λ_{em} (nm). Stokes shifts $\Delta\nu_{ST}$ (cm^{-1}). fluorescence quantum yields Φ_f. fluorescence lifetimes τ_f (ns). radiative k_f (10^8 s^{-1}) and nonradiative $k_{nr} = (1 - \Phi_f)/\tau_f$ (10^8 s^{-1}) rate constants; Bu_2O: n-dibutylether. Et_2O: ethylic ether. AcOEt: ethyl acetate. DCM: dichloromethane. DCE: 1.2-dichloroethane. ACN: acetonitrile.