Supplementary Material (ESI) for Chemical Communications

Supporting information for:

Synthesis of chromophores combining second harmonic generation and two photon induced fluorescence properties.

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Characterisations of 1 and 2.

4-(2'-(*N*,*N*-dihexyl-pheny)ethynyl-2,6-di(diethylcarbamoyl)-pyridine 1. Mp = 101.6°C. ^{1}H NMR (CD_3CN) : δ = 7.47 (s, 2H); 7.35 (d, 2H, *J* = 9 Hz); 6.64 (d, 2H, *J* = 9 Hz); 3.48 (q, 4H, *J* = 7 Hz) ; 3.3 (m, 4H); 3.3 (m, 4H); 1.55 (m, 4H); 1.3 (m, br, 12H); 1.18 (t, 6H, *J* = 7 Hz) ; 1.08 (t, 6H, *J* = 7 Hz) ; 0.88 (t, 6H, *J* = 6 Hz). ^{13}C NMR (CD_3CN) : δ = 166.9; 154.2; 148.6; 133.8; 132.9; 122.2; 110.9; 105.7; 97.4; 84.0 ; 49.9; 42.4; 39.0; 30.9; 26.3 ; 25.8; 21.9; 13.1; 11.6; 12.8. FTIR 2203 cm^{-1} ($\nu_{C\equiv C}$); 1625 cm^{-1} ($\nu_{C=O}$). Elemental analysis calcd (%) for $C_{35}H_{52}N_4O_2$: C 74.96, H 9.35, N: 9.99; found: C 75.04, H 9.38, N 9.78.

4-(2'-(*N*,*N*-dihexyl-7'-amino-9',9'-dihexylfluorene)ethynyl-2,6-di(diethylcarbamoyl)-pyridine 2. ^{1}H NMR ($CDCl_3$, δ) 7.68 (s, 2H), 7.51-7.38 (m, 4H), 6.59 (d, 1H, *J = 8.6 Hz*), 6.54 (s, 1H), 3.55 (q, 4H, *J = 7.1 Hz*), 3.48-3.32 (m, 8H), 1.94-1.82 (m, 4H), 1.68-1.50 (m, 4H), 1.46-0.96 (m, 36H), 0.91-0.83 (m, 6H), 0.79-0.72 (m, 10H); ^{13}C NMR ($CDCl_3$, δ) 167.73, 153.77, 153.08, 149.91, 148.68, 143.83, 134.31, 131.21, 127.98, 126.00, 125.09, 121.09, 117.87, 116.85, 110.86, 105.99, 98.04, 85.67, 54.79, 51.46, 43.27, 40.57, 40.15, 31.76, 31.51, 29.75, 27.23, 26.86, 23.71, 22.65, 14.27, 14.03, 12.78 ; FTIR 2202 cm^{-1} ($\nu_{C\equiv C}$); 1640 cm^{-1} ($\nu_{C=O}$). Elemental analysis calcd (%) for $C_{54}H_{80}N_4O_2.2H_2O$: C 76.01; H 9.92; N 6.57; found C 76.49; H 9.69; N 6.26.

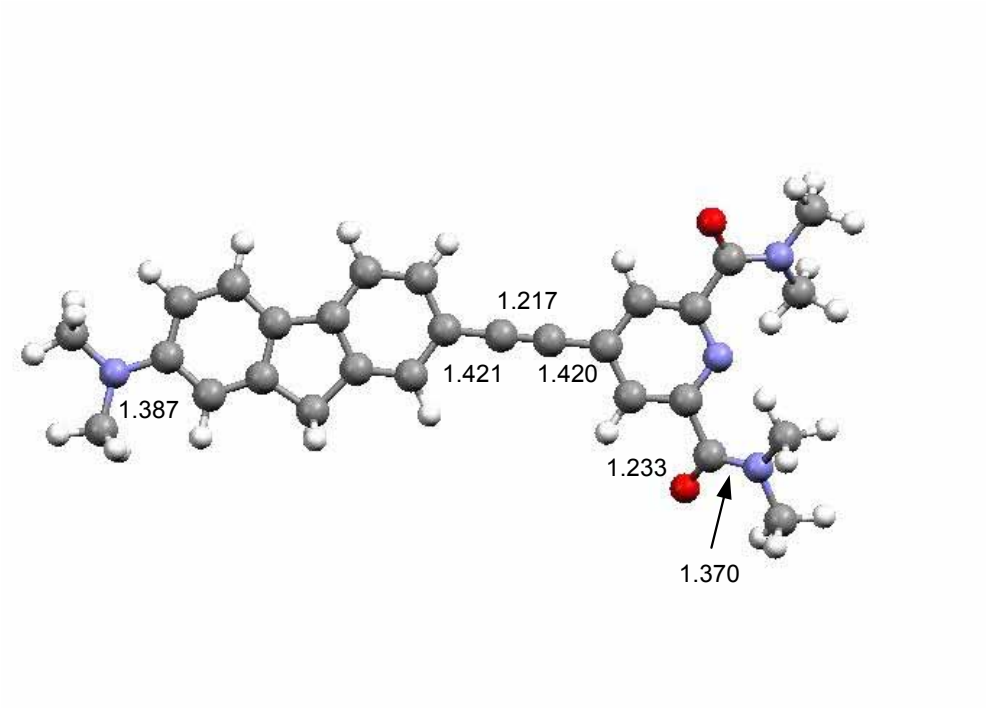

Fig S1. Optimized geometry of **2'** at the B3LYP/6-31G* level of Denstity Functional Theory. The optimized AM1 geometry has been used as guess. Selected bond lengths are given in Angröms.

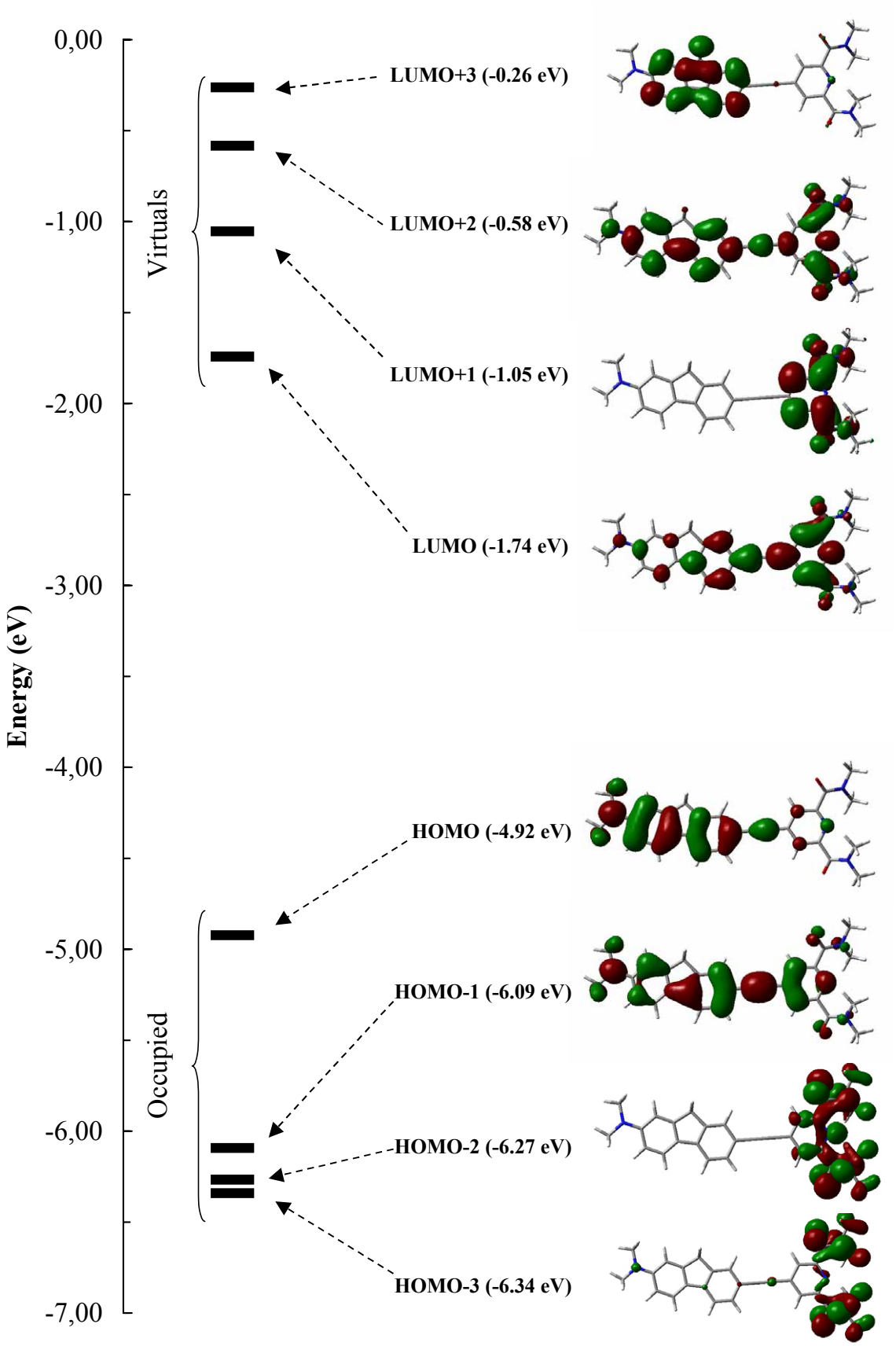

Fig S2. Khon-Sham orbitals diagram of **2'** in its optimized geometry (fig S1).

Table S1. Excitation spectrum of **2'** in its optimized geometry (fig S1) calculated at the B3LYP/6-31G* level of Time-Dependent Density Functional Theory. C represents the coefficient of the current configuration in the current excited state.

Excitation	Main contributions			Energy (eV)	Wavelength (nm)	Oscillator strength
	Configuration	C	C^2			
1	**HOMO →LUMO**	**0.67**	**0.45**	2.93	422	1.02
2	**HOMO →LUMO+1**	**0.69**	**0.48**	3.53	351	0.00
3	**HOMO-2→LUMO**	**0.62**	**0.38**	3.87	320	0.01
	HOMO-4 →LUMO	0.21	0.04			
	HOMO-8 →LUMO	-0.13	0.02			
4	**HOMO-1→LUMO**	**0.50**	**0.25**	3.93	315	0.65
	HOMO →LUMO+2	0.38	0.14			
	HOMO-3 →LUMO	0.19	0.04			
	HOMO →LUMO+3	0.12	0.01			
	HOMO-6 →LUMO	0.11	0.01			
5	**HOMO →LUMO+3**	**0.45**	**0.20**	3.94	314	0.03
	HOMO-3→LUMO	**0.42**	**0.18**			
	HOMO →LUMO+2	0.21	0.04			
	HOMO-7 →LUMO	0.13	0.02			
	HOMO-6 →LUMO	0.11	0.01			
6	**HOMO →LUMO+3**	**0.45**	**0.20**	4.01	309	0.19
	HOMO-3→LUMO	**0.43**	**0.18**			
	HOMO →LUMO+2	-0.20	0.04			
	HOMO-1 →LUMO	-0.14	0.02			
	HOMO-7 →LUMO	0.12	0.01			
7	**HOMO-4→LUMO**	**0.60**	**0.36**	4.04	307	0.01
	HOMO-2 →LUMO	-0.26	0.07			
	HOMO-1 →LUMO+1	-0.10	0.01			
8	**HOMO →LUMO+2**	**0.43**	**0.18**	4.08	304	0.01
	HOMO-1 →LUMO	-0.33	0.11			
	HOMO-3 →LUMO	0.25	0.06			
	HOMO-6 →LUMO	-0.19	0.04			
	HOMO →LUMO+3	-0.12	0.01			
	HOMO-4 →LUMO	0.11	0.01			
9	**HOMO-6→LUMO**	**0.54**	**0.29**	4.13	300	0.00
	HOMO-2 →LUMO+1	-0.24	0.06			
	HOMO-1 →LUMO	-0.20	0.04			
	HOMO-4 →LUMO+1	-0.15	0.02			
	HOMO →LUMO+2	0.13	0.02			
	HOMO-6 →LUMO+2	0.12	0.01			
10	**HOMO-5→LUMO**	**0.56**	**0.31**	4.15	299	0.00
	HOMO →LUMO+4	0.33	0.11			
	HOMO-7 →LUMO	-0.13	0.02			
	HOMO-5 →LUMO+4	-0.12	0.01			

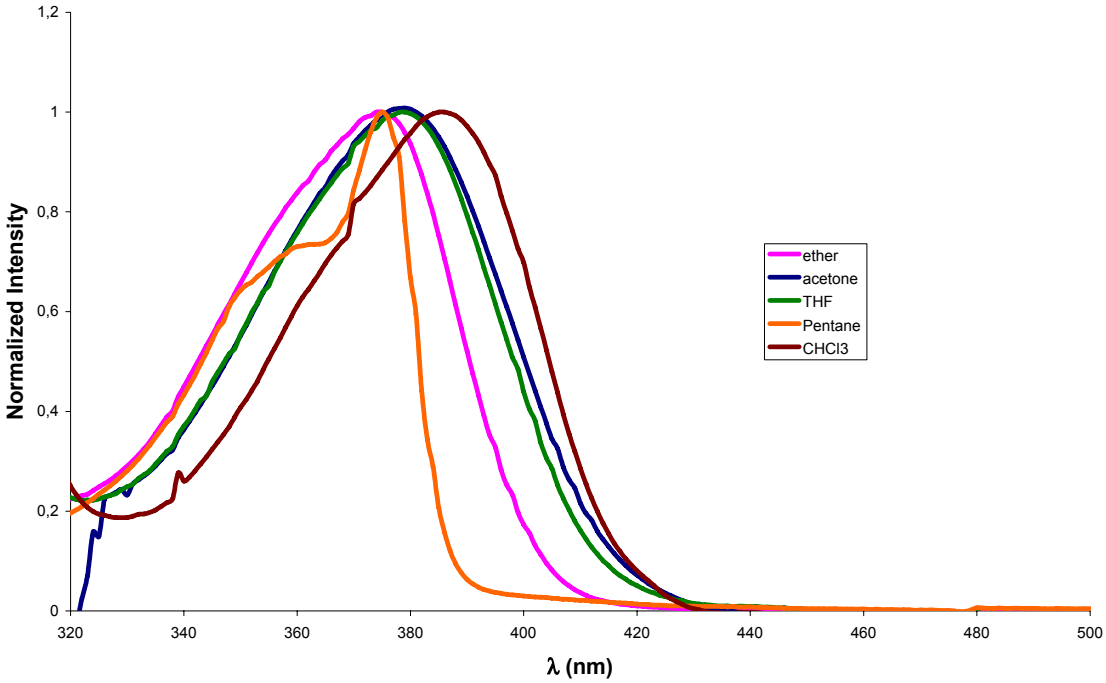

Fig S3. Solvatochromism in absorption in the case of **1**.

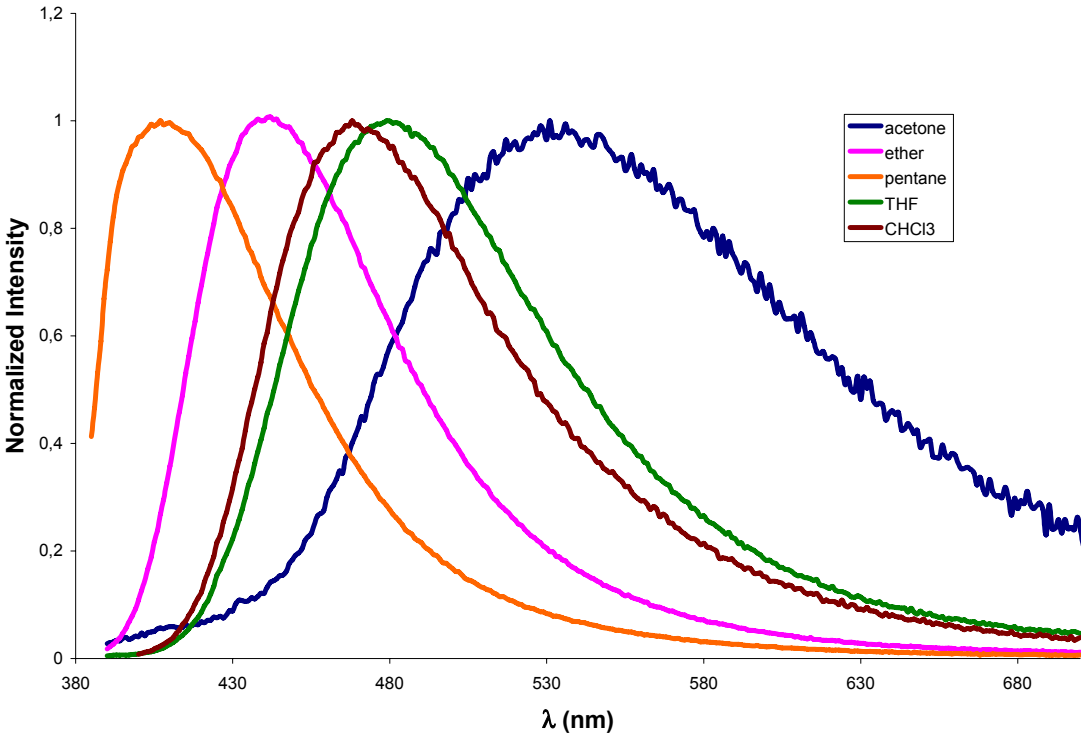

Fig S4. Solvatochromism in emission in the case of **1**.

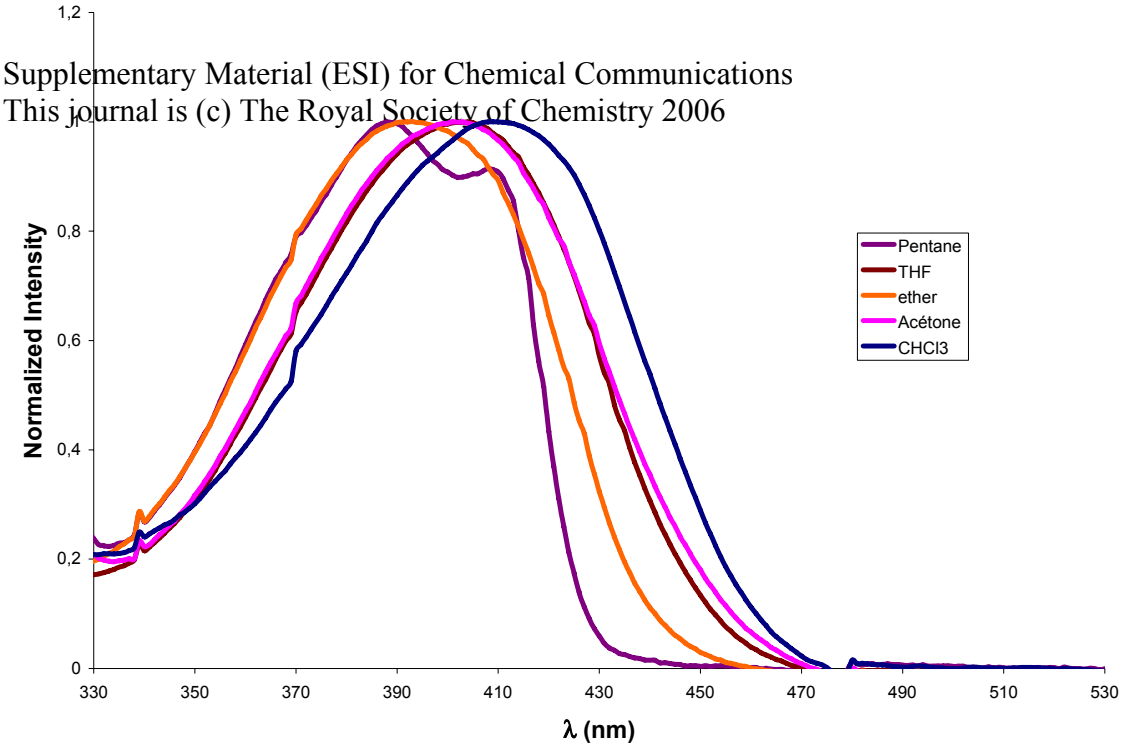

Fig S5. Solvatochromism in absorption in the case of **2**.

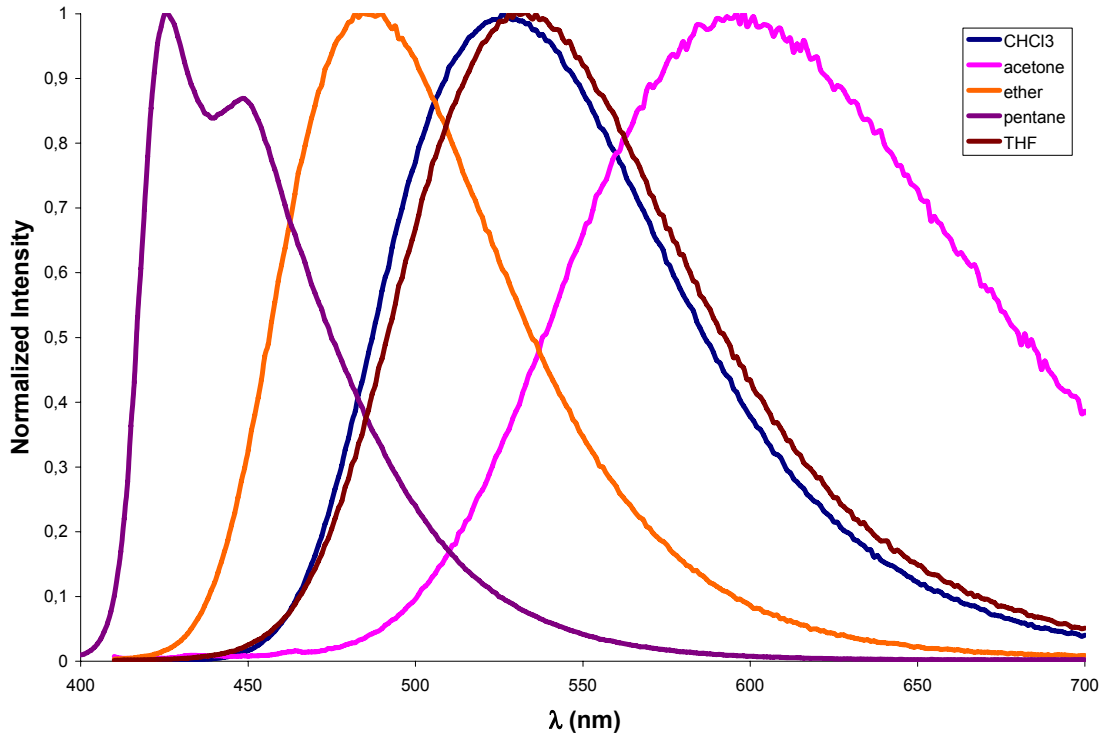

Fig S6. . Solvatochromism in emission in the case of **2**.