Electronic Supplementary Information

Figure S1; Tables S1-S3.

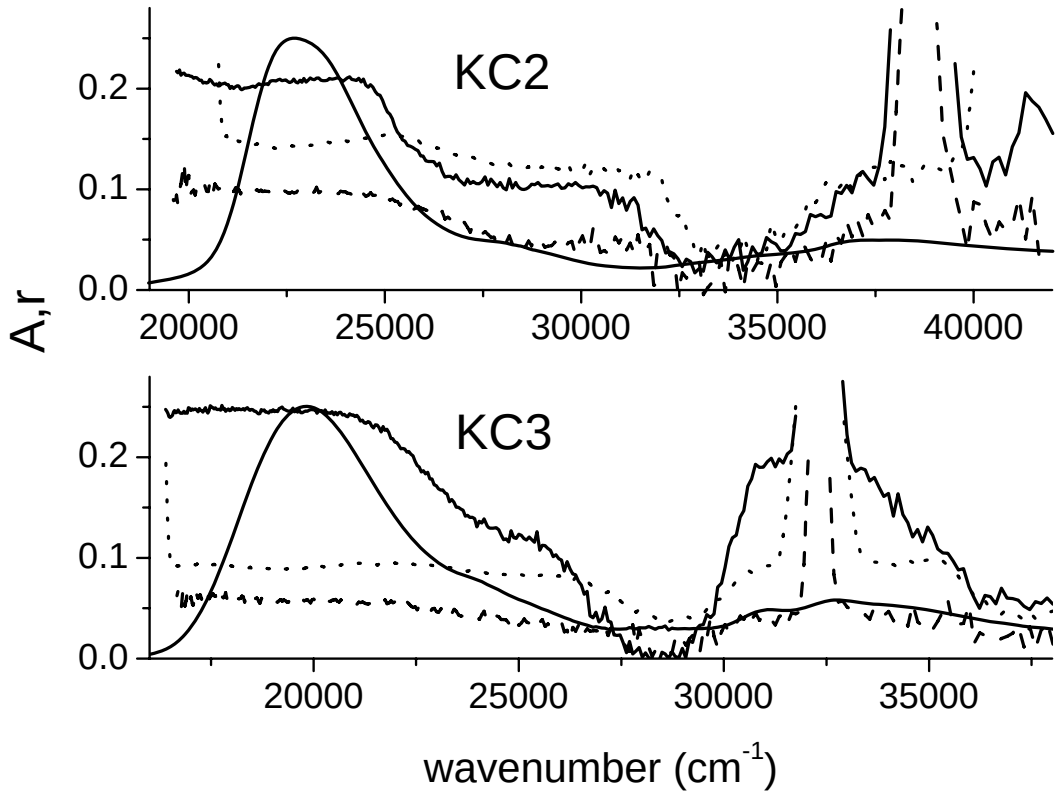

Figure S1. Absorption spectra in acetonitrile (A=absorbance) and excitation anisotropy (r) spectra of KC2 and KC3 in 1-pentanol (solid), acetonitrile (dotted) and dichloromethane (dashed). Monitoring wavelengths were, respectively: 530, 490 and 530 nm for KC2, and 620 nm for KC3.

Table S1. Properties of the ground and of the 20 lowest-lying singlet excited states of KC2 calculated at the DT DFT - B3LYP/6-31G** level. The state energies (column 2) are referred to the ground state. μ_y^i: y-components of the permanent dipole moments; $\mu_{x,y,z}^{0\to i}$: components of the 0→i transition dipole moments ($\mu^{0\to i}$); *f*: 0→i transition oscillator strengths.

State Index	*E*/eV	μ_y^i/D	$\mu_x^{0\to i}$/D	$\mu_y^{0\to i}$/D	$\mu_z^{0\to i}$/D	$\mu^{0\to i}$/D	*f*
0	–	2.637	–	–	–	–	–
1	3.1379	-1.145	0.000	0.000	0.000	0.000	0.000
2	3.2806	5.292	-10.765	0.000	0.000	10.765	1.442
3	3.6521	3.893	0.000	0.820	0.000	0.820	0.009
4	4.7936	1.934	-6.004	0.000	0.000	6.004	0.655
5	4.8963	-3.025	0.000	0.000	0.057	0.057	0.000
6	4.9345	3.544	0.000	-0.157	0.000	0.157	0.000
7	5.4144	3.085	0.000	-0.082	0.000	0.082	0.000
8	5.6373	4.608	0.900	0.000	0.000	0.900	0.017
9	6.0552	2.509	0.000	0.000	0.000	0.000	0.000
10	6.0604	2.427	0.000	0.000	-0.537	0.537	0.007
11	6.1527	3.654	-1.846	0.000	0.000	1.846	0.079
12	6.3846	2.750	0.000	-0.941	0.000	0.941	0.021
13	6.4763	-2.379	0.000	0.000	0.000	0.000	0.000
14	6.5486	-0.967	0.000	0.000	0.000	0.000	0.000
15	6.5760	-1.090	0.000	0.000	-0.774	0.774	0.015
16	6.6846	1.218	0.000	0.000	0.294	0.294	0.002
17	6.6851	1.346	0.000	0.000	0.000	0.000	0.000
18	6.7145	2.672	0.000	0.000	0.094	0.094	0.000
19	6.7268	2.129	-0.287	0.000	0.000	0.287	0.002
20	6.8417	3.379	0.000	-0.157	0.000	0.157	0.001

Table S2. Properties of the ground and of the 20 lowest-lying singlet excited states of KC3 calculated at the DT DFT - B3LYP/6-31G** level. See the caption to Figure S1 for explanatory details.

State Index	E/eV	μ_y^i/D	$\mu_x^{0\to i}$/D	$\mu_y^{0\to i}$/D	$\mu_z^{0\to i}$/D	$\mu^{0\to i}$/D	f
0	–	2.322	–	–	–	–	–
1	2.7619	4.711	13.610	0.000	0.000	13.610	1.940
2	2.9240	-1.462	0.000	0.000	0.000	0.000	0.000
3	3.0844	3.762	0.000	0.620	0.000	0.620	0.004
4	3.9523	2.042	8.227	0.000	0.000	8.227	1.015
5	4.1333	3.288	0.000	0.336	0.000	0.336	0.002
6	4.3280	-3.340	0.000	0.000	-0.056	0.056	0.000
7	4.5671	2.605	0.000	-0.114	0.000	0.114	0.000
8	4.6273	4.083	-1.726	0.000	0.000	1.726	0.052
9	5.1171	2.737	2.900	0.000	0.000	2.900	0.163
10	5.3054	2.687	0.000	0.975	0.000	0.975	0.019
11	5.5875	2.199	0.649	0.000	0.000	0.649	0.009
12	5.6210	2.897	0.000	-0.022	0.000	0.022	0.000
13	5.6529	-2.798	0.000	0.000	0.000	0.000	0.000
14	5.9014	2.906	0.000	0.000	0.000	0.000	0.000
15	5.9018	2.893	0.000	0.000	-0.487	0.487	0.005
16	5.9883	3.218	0.000	0.828	0.000	0.828	0.016
17	6.1739	3.981	0.272	0.000	0.000	0.272	0.002
18	6.2536	3.036	0.000	0.156	0.000	0.156	0.001
19	6.2588	2.472	0.101	0.000	0.000	0.101	0.000
20	6.2863	0.247	0.000	0.000	0.000	0.000	0.000

Table S3. Polarizabilities, $\langle\alpha\rangle$ (x10^{24}cm^3), and two-level-term contributions to the first hyperpolarizabilities (x10^{30}cm^{5}esu^{-1}) of KC2 and KC3 from TD DFT SOS calculations expanded over the 20 lowest-lying singlet excited states.

	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	$\beta_{yyy,2}$	$\beta_{yxx,2}$	$\beta_{yzz,2}$	$\beta_{y,2}$
KC2	54.37	0.42	0,19	18.33	0.16	21.53	–0. 04	21.65
KC3	108.07	0.56	0.05	36.23	0.22	44.55	2x10^{-3}	44.78