Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic supplementary information

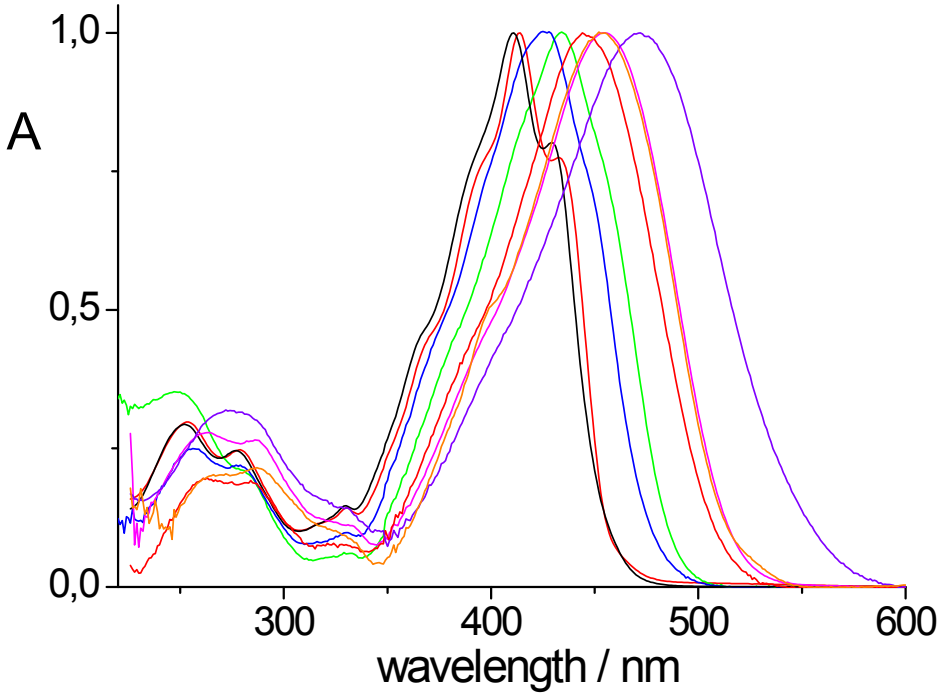

Figure S1. Normalized UV-visible absorption spectra of KM1 in (maxima from left to right) n-hexane, cyclohexane, diethyl ether, 1,4-dioxane, acetonitrile, chloroform, dichloromethane, methanol.

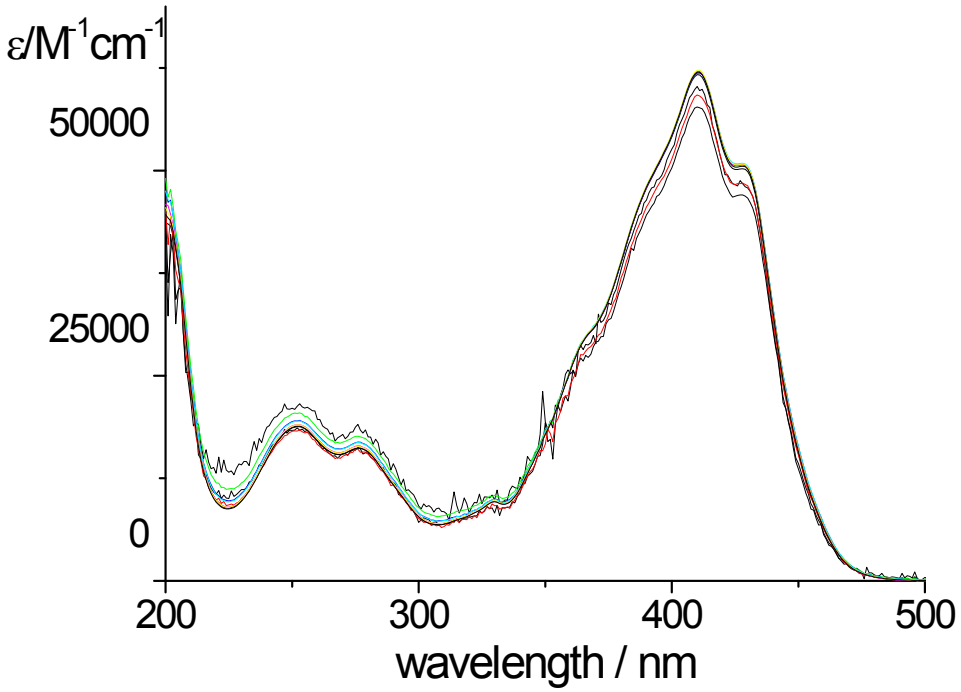

Figure S2. UV-visible absorption spectrum of KM1 in n-hexane measured at 10 concentrations between 70 nM and 24 μM.

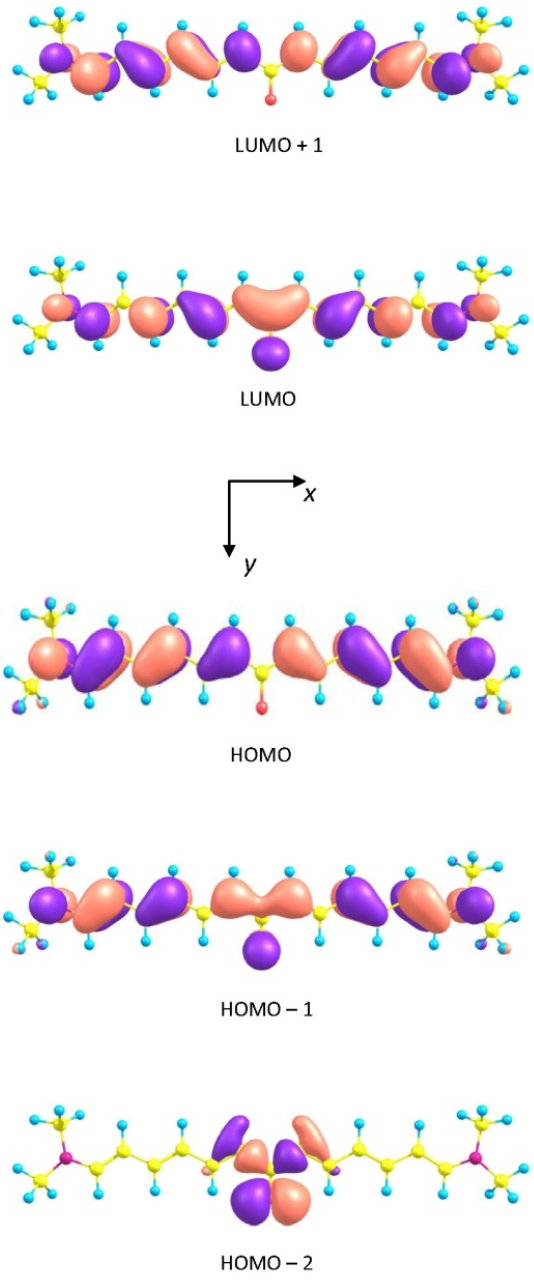

Figure S3 Pictures of selected MOs of KC3

Table S1. Properties of $^1\pi\pi^*$ states within the first 30 excited states of KM1, calculated at the TDDFT-B3LYP/6-31G** level and used in the SOS calculations. Labels indicate the serial number of each $^1\pi\pi^*$ state in the general excited state set. State energies (and symmetries) are given in column one. The diagonal elements are the state y-directed dipole moments (in D). The other elements are the transition dipole moments (in D). Polarizations are specified in the last column. For the first 9x9 block see Table 6 of the text.

E/eV	No	11	12	13	14	17	18	19	20	21	22	23	24	25	27	Pol.
0		-2.757			-1.546	-1.737	-1.034			0.840		-2.083			1.505	x
1 $^1A_1$	**0**		0.612	-0.751				-0.301	-1.019		0.807		0.439	-0.230		y
2.977			4.262	-1.028				-1.040	-0.327		-0.339		0.143	-0.683		x
1 $^1B_2$	**1**	1.854			-0.146	1.783	-1.423			-0.155		-0.449			1.041	y
3.336		-7.927			-2.266	5.023	0.092			0.304		0.709			-0.976	x
2 $^1A_1$	**3**		-0.402	-1.527				-1.404	-0.875		-1.108		1.294	1.021		y
4.288		1.227			-1.922	-8.532	-3.690			5.632		3.320			-1.178	x
3 $^1A_1$	**4**		1.040	-0.515				-0.996	1.570		2.081		0.175	0.387		y
4.310			-10.908	0.750				9.939	-7.671		0.073		-1.877	-0.468		x
2 $^1B_2$	**5**	0.028			-1.173	1.284	2.788			0.064		-1.423			-0.408	y
4.408			-5.672	-6.054				-15.904	-4.548		1.307		-3.647	2.171		x
3 $^1B_2$	**6**	0.725			0.157	-2.192	-1.439			-1.815		-1.020			0.303	y
4.446		-10.783			-1.122	-11.619	2.731			-5.708		-1.557			-2.595	x
4 $^1A_1$	**7**		0.469	0.443				-1.319	-1.255		0.888		-1.760	0.877		y
4.706		-12.915			5.336	10.910	8.576			5.908		1.288			-6.632	x
5 $^1A_1$	**8**		2.161	-0.918				1.688	-0.974		-0.469		-0.658	3.878		y
4.745			3.329	24.507				-4.160	-2.807		10.265		0.781	-5.908		x
4 $^1B_2$	**9**	0.890			-1.918	-0.236	0.232			0.997		0.956			1.420	y
4.760		6.762	6.872	-12.510				-6.271	5.287		0.798		-11.755	-7.282		x
5 $^1B_2$	**11**				-0.403	-0.129	0.420			0.360		0.186			2.606	y
4.786			7.388	-0.906	27.615	-7.061	-1.812			6.470		-9.225			0.239	x
6 $^1A_1$	**12**							-0.264	-0.549		0.566		-0.660	-0.610		y
4.846				5.518	28.474	0.928	1.588			-2.366		6.643			-0.529	x
7 $^1A_1$	**13**							0.130	1.266		0.605		1.461	-0.071		y
4.866					6.168	0.160	0.048	-2.577	-0.415		-6.747		-1.087	1.803		x
6 $^1B_2$	**14**									-1.169		-2.101			-0.281	y
5.662						5.156	-2.125	16.759	2.874		2.953		-1.769	-4.164		x
7 $^1B_2$	**17**									0.301		-0.542			-0.055	y
5.837							3.830	-3.489	-8.666		-7.019		14.991	-3.684		x
8 $^1B_2$	**18**									1.424		0.370			0.774	y
5.842								5.560	0.939	0.326		0.881			-0.471	x
8 $^1A_1$	**19**										-0.072		-0.529	0.441		y
5.937									4.763	13.572		-12.429			-1.088	x
9 $^1A_1$	**20**										-1.817		0.437	0.366		y
5.964										7.814	-18.054		-3.514	-0.199		x
9 $^1B_2$	**21**											0.250			-0.138	y
6.022											6.637	0.588			-1.595	x
10 $^1A_1$	**22**												-1.710	0.842		y
6.102												3.116	0.548	0.288		x
10 $^1B_2$	**23**														-0.563	y
6.144													3.665	0.834	-2.433	x
11 $^1A_1$	**24**															y
6.201														8.147	-21.418	x
12 $^1A_1$	**25**															y
6.349															8.837	
11 $^1B_2$	**27**															

Table S2. Values of δ_{TP} (10^5 au) and σ_{TP} (GM) calculated for the $g \rightarrow e$ transition neglecting the S_{yy} element of the TPA tensor, i.e. using the expression $\delta_{TP}=6\times S_{xx}^2$

	KM1		KC3		KC2	
	δ_{TP}	σ_{TP}	δ_{TP}	σ_{TP}	δ_{TP}	σ_{TP}
a'	190.5	5.52x10^3	332.8	8.80x10^3	109.1	3.69x10^3
a	206.0	5.60x10^3	478.4	11.09x10^3	103.5	3.37x10^3
b	142.8	3.88x10^3	281.8	6.53x10^3	64.6	2.10x10^3
c	134.4	3.65x10^3	281.3	6.52x10^3	64.0	2.08x10^3
d	135.3	3.68x10^3				
e	55.2	1.50x10^3	92.3	2.14x10^3	20.1	0.65x10^3

Table S3. Values of $\left[\sigma_{TP}^{g\rightarrow c}/\sigma_{TP}^{g\rightarrow e}\right]$x100 for KM1, KC3 and KC2 derived from the data of Tables 9,10.

Method/ calculation	KM1	KC3	KC2
TSM/*a'*	10.5	2.2	4.1
TDDFT-SOS/*c*	2.4	0.5	1.2
Response Theory/*e*	1.5	0.3	0.8