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

The Influence of the Aggregation on the Third-order Nonlinear Optical Property of the π-Conjugated Chromophores: the Case of Cyanine Dyes

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Content

Table S1. The geometric parameters ϑ (°), *d* (Å) and *D* (Å) of the P, H and J dimers of the HR1101 and HR1161 calculated at the ωB97XD/cc-pVDZ level in gas phase and PCM solvation.

Compound	Configuration	external environment	P dimer			H dimer			J dimer		
			ϑ	*d*	*D*	ϑ	*d*	*D*	ϑ	*d*	*D*
HR1101	Cis	Gas	68.1	3.397	~0	7.8	3.648	~0	29.1	3.562	7.075
	Cis	PCM	52.2	3.243	~0	16.1	3.745	~0	27.8	3.341	8.288
	Trans	Gas					3.513	~1.000		3.428	8.985
	Trans	PCM					3.295	~1.000		3.523	8.146
	Cis-Trans	Gas					3.374	~2.000		3.558	7.518
	Cis-Trans	PCM					3.433	~3.000		3.482	7.823
HR1161	Cis	Gas	79.9	3.661	~1	6.9	3.637	~0	4.2	3.353	8.414
	Cis	PCM				6.6	3.461	~0	~0	3.361	8.880
	Trans	Gas					3.235	~0		3.506	8.295
	Trans	PCM					3.577	~0		3.520	7.723
	Cis-Trans	Gas					3.521	~1.500		3.431	5.182
	Cis-Trans	PCM					3.503	~2.800		3.414	6.461

Table S2. The IP-tuned and PCM-tuned optimal ω values for the isolated cyanines, cyanine complexes and cyanine dimers of the HR1101 and HR1161.

Compound	Configuration	external environment	Isolated cyanine	Cyanine complex	Cyanine dimer		
					P	H	J
HR1101	Cis	GAS	0.106	0.192	0.099	0.116	0.115
	Cis	PCM		0.001	0.001	0.001	0.001
	Trans	GAS	0.106				
	Trans	PCM		0.001	0.001	0.001	0.001
	Cis-Trans	GAS					
	Cis-Trans	PCM		0.001	0.001	0.001	0.001
HR1161	Cis	GAS	0.111	0.176	0.093	0.110	0.128
	Cis	PCM		0.001	0.001	0.001	0.001
	Trans	GAS	0.110				
	Trans	PCM		0.001	0.001	0.001	0.001
	Cis-Trans	GAS					
	Cis-Trans	PCM		0.001	0.001	0.001	0.001

Table S3. The components of the γ (10^{-33} esu) and the $\langle\gamma\rangle$ (10^{-33} esu) calculated at the ωB97XD^{IP}/6-31+G(d) level for the isolated cyanine and at the ωB97XD^{PCM}/6-31+G(d) level for the cyanine dimers.

Compound	Configuration	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{xxzz}	γ_{yyzz}	$\langle\gamma\rangle$
HR1101	Cis-Isolated cyanine	-2.44	0.03	0.02	0.06	0.03	0.01	-0.44
	Cis-Cis-P	0.33	0.29	0.27	-0.07	-0.02	0.33	0.27
	Cis-Cis-H	1.52	2.19	0.41	0.27	0.14	0.76	1.29
	Cis-Cis-J	23.77	1.50	0.09	2.00	0.60	0.13	6.16
	Trans-Isolated cyanine	-1.37	0.06	0.02	0.08	0.02	0.01	-0.22
	Trans-Trans-H	0.52	0.39	0.29	0.18	0.12	0.22	0.44
	Trans-Trans-J	4.02	0.19	0.11	0.26	0.48	0.04	1.18

	Cis-Trans- H	1.00	1.02	0.35	0.82	0.36	0.18	1.02
	Cis-Trans- J	9.73	1.60	0.11	1.28	0.58	0.05	3.05
	Cis-Isolated cyanine	-1.52	0.04	0.02	0.08	0.03	0.01	-0.25
	Cis-Cis-P	0.69	0.56	0.06	0.24	0.10	0.08	0.44
	Cis-Cis-H	2.19	4.47	0.10	1.73	0.09	0.08	2.11
	Cis-Cis-J	24.87	2.45	0.15	3.23	1.07	0.20	7.30
HR1161	Trans-Isolated cyanine	-0.83	0.10	0.02	0.11	0.02	0.01	-0.09
	Trans-Trans-H	0.56	0.28	0.62	0.19	0.07	0.15	0.45
	Trans-Trans-J	2.17	0.23	0.07	0.31	0.14	0.03	0.68
	Cis-Trans- H	1.34	1.16	0.36	0.88	0.40	0.22	1.17
	Cis-Trans- J	14.06	2.12	0.11	3.17	0.62	0.11	4.82