

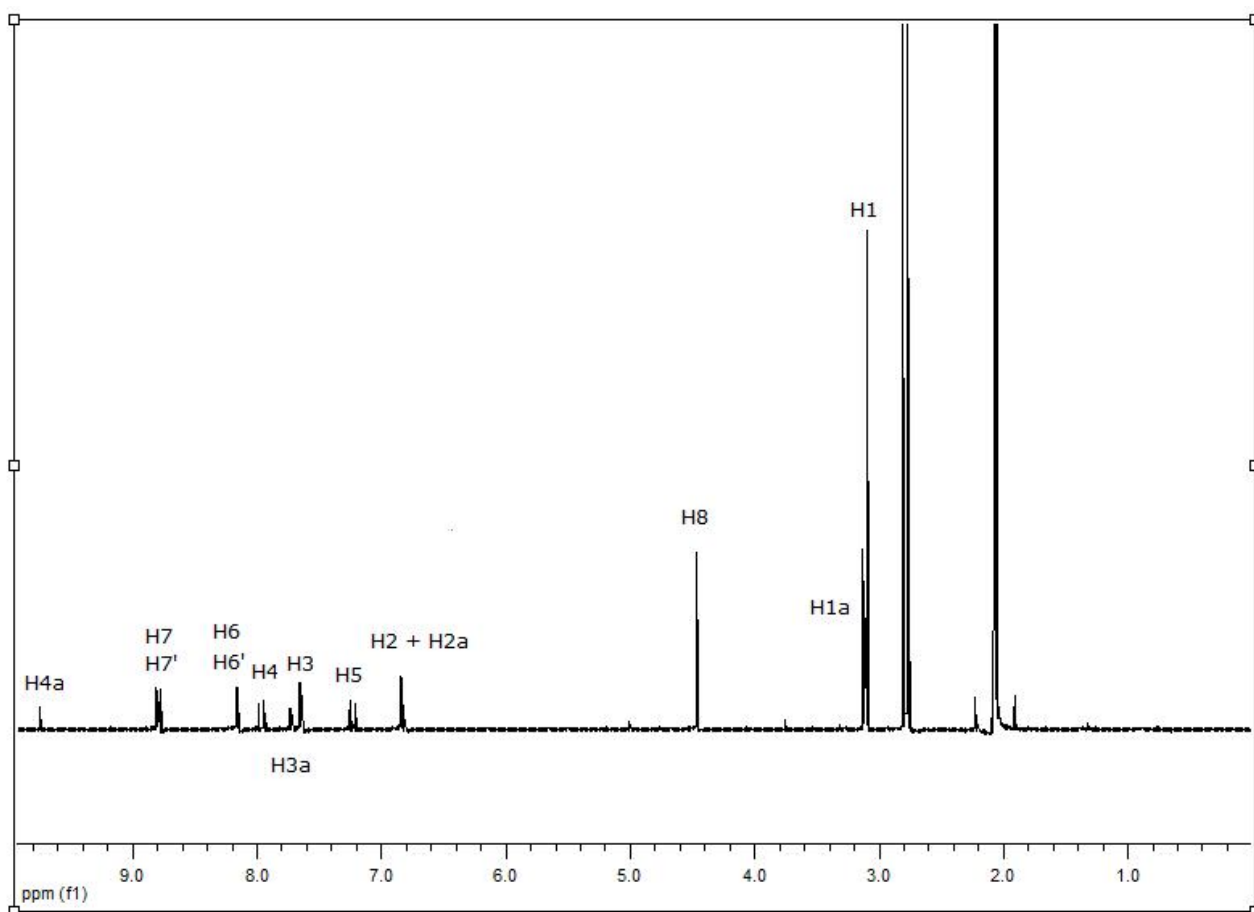
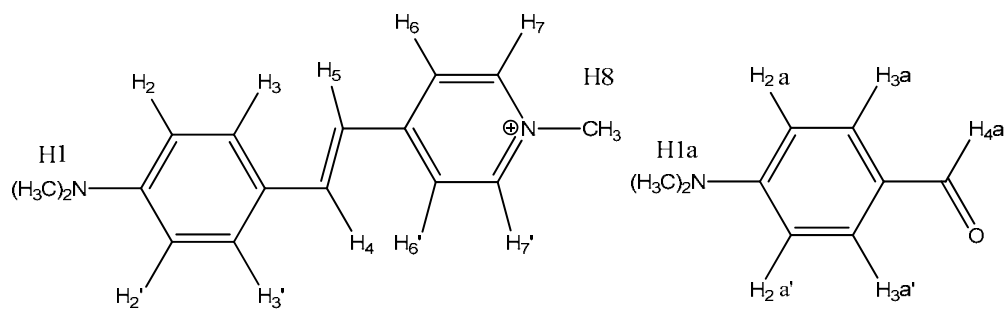
**Stabilization through *p*-dimethylaminobenzaldehyde of a new NLO-active phase of [*E*-4-(4-dimethylaminostyryl)-1-methylpyridinium] iodide: synthesis, structural characterization and theoretical investigation of its electronic properties**

Francesca Nunzi,<sup>a</sup> Simona Fantacci,<sup>b\*</sup> Elena Cariati,<sup>c\*</sup> Elisa Tordin,<sup>c</sup> Nicola Casati<sup>d</sup> and Piero Macchi<sup>d,e\*</sup>

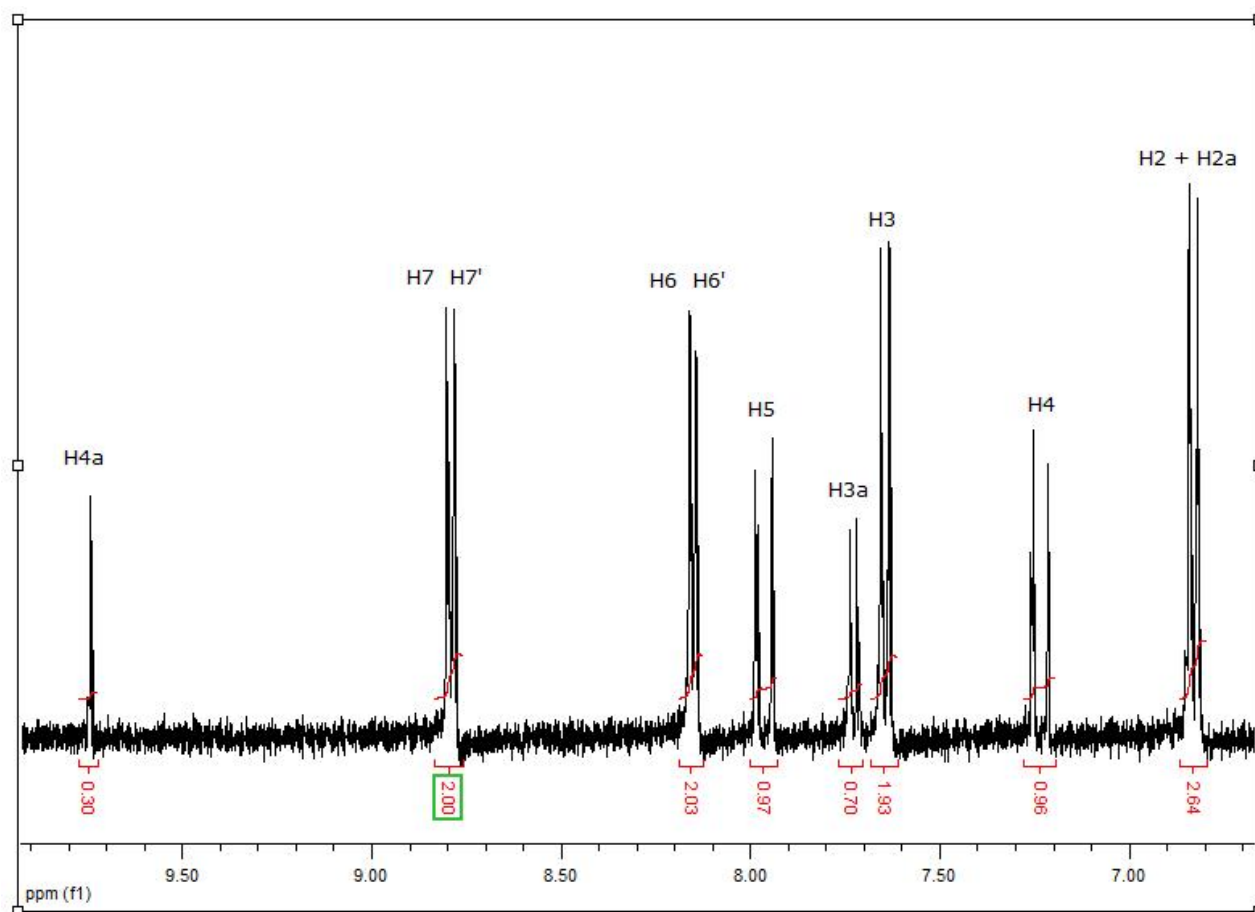
<sup>a</sup> Dipartimento di Chimica, Università degli Studi di Perugia, via Elce di Sotto 8, I-06123 Perugia, Italy. <sup>b</sup> Istituto CNR di Scienze e Tecnologie Molecolari (ISTM-CNR), c/o Dipartimento di Chimica, Università degli Studi di Perugia, via Elce di Sotto 8, I-06123 Perugia, Italy. <sup>c</sup> Dipartimento di Chimica Inorganica, Metallorganica e Analitica “Lamberto Malatesta” dell’Università degli Studi di Milano and UdR dell’INSTM di Milano, via Venezian 21, 20133 Milano, Italy. <sup>d</sup> Dipartimento di Chimica Strutturale e Stereochimica Inorganica and Centro di Eccellenza CIMAINA dell’Università degli Studi di Milano, via Venezian 21, 20133 Milano, Italy. <sup>e</sup> Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

## Supporting Information

$^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 400.1 MHz, 298 K):



ppm	Multiplicity (J Hz)	Integral	Assignment
9.74	s	0.30	H4a
8.80	d (6.8)	2.00	H7 H7'
8.16	d (6.8)	2.03	H6 H6'
7.97	d (16.0)	0.97	H5
7.72	d (8.9)	0.70	H3a
7.65	d (9.0)	1.93	H3
7.24	d (16.0)	0.96	H4
6.83	m	2.64	H2+H2a
4.46	s	2.80	H8
3.12	s	1.89	H1a
3.09	s	5.40	H1



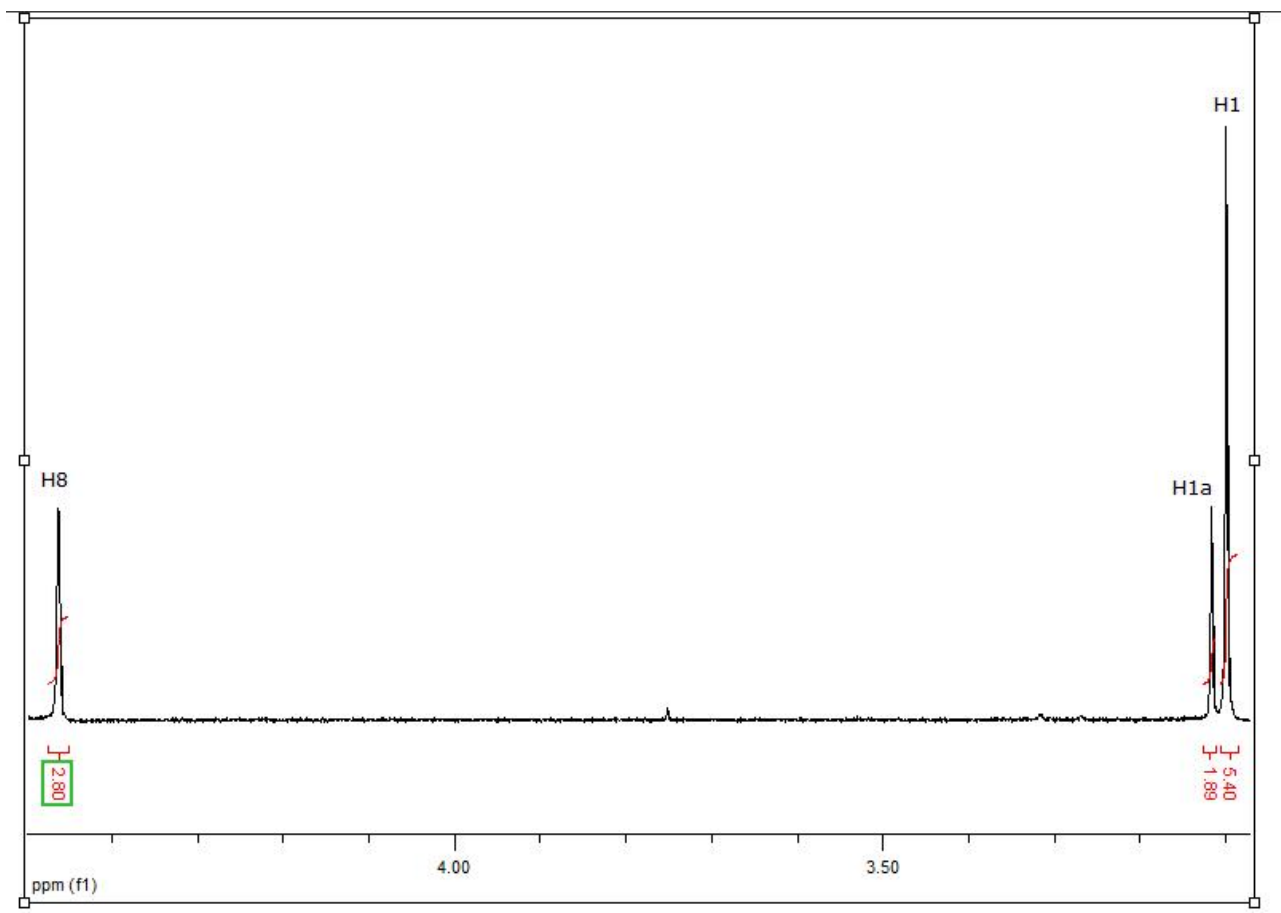


Table S1: Lowest excitation energies (eV) and oscillator strengths (in parentheses) for the [DAMS]<sup>+</sup> monomer and dimer calculated at different levels of theory. The experimental absorption maximum of the [DAMS]<sup>+</sup> is 471 nm (2.633 eV).

	BP86	LB94	B3LYP	BHandH	CC2
MONO	2.496	2.395	2.696	2.902	2.342
S0→S1	(1.122)	(1.078)	(1.376)	(1.587)	(1.627)
DIME	1.297	1.238	1.877	2.646	2.125
S0→S1	(0.023)	(0.018)	(0.037)	(0.030)	(0.001)

We carried out calculations with BP86/TZP, LB94/TZP, B3LYP/6-31g(d,p) and BHandH/6-31g(d,p) XC functionals and basis sets. A benchmark second order approximate coupled cluster (CC2) calculation as implemented in TURBOMOLE program package<sup>1,2</sup> was also performed on the same systems, see Table S1. The results for the monomer show that B3LYP provides an excellent agreement with the available experimental data (2.633 eV), while pure GGA functionals give red-shifted absorptions by ca. 0.1-0.2 eV. BHandH, which contains an increased amount of Hartree-Fock exchange with respect to B3LYP (50% vs. 20%), provides on the other hand rigidly blue-shifted values compared to the experiment, by ca. 0.3 eV. The CC2 excitation energy is consistent with GGA results, i.e. ca. 0.2 eV red-shifted compared to the experiment.

Moving to the dimer, it is interesting to notice that a H→L dark excitation is computed as the lowest excited state at all levels of calculation, even though, as already observed for the monomer, at different energy, depending on the level of theory. This is different from what previously found,<sup>3</sup> in which several spurious excited states were found to appear below the main optical transition when using GGA functionals and in some cases also hybrid functionals. Of particular significance is the fact that both BHandH and CC2 results predict the presence of this excited state, with the CC2 results being close to the B3LYP excitation energy (they differ by ca. 0.2 eV). Considering the analysis above and the overall good agreement with the experiment, both for the monomer and for various aggregates, we can thus conclude that our results are sufficiently accurate for the goal of the present investigation.

- 1 (a) Hättig, C.; Weigend, F., *J. Chem. Phys.* 2000, **113**, 5154; (b) Hättig, C.; Hellweg, A.; Kähn, A., *Phys. Chem. Chem. Phys.* 2006, **8**, 1159-1169.
- 2 Alhrichs, R.; al., e. TURBOMOLE v. 5.10, University of Karlsruhe, Germany;
- 3 R.J. Magyar, S: Tretiak *J. Chem. Theory. Comput.* 2007, **3**, 976.

**Table S2:** Excitation energy (E), oscillator strength (f) and composition of the lowest singlet excited states for the fish-bone 2 aggregate computed at B3LYP(6-31G(d,p)) level of theory.

	E (eV)	E (nm)	F	MOs
1	1.8221	680	0.0419	58%(H-5→L+1)+37%(H-6→L+1)
2	2.1042	589	0.0446	67%(H-5→L+2)+30%(H-6→L+2)
3	2.2714	546	0.0485	50%(H-2→L+8)+27%(H-2→L+9)+13%(H-1→L+8)+6%(H-1→L+9)
4	2.3255	533	0.0152	90%(H-7→L+1)+7%(H-9→L)
5	2.3307	532	0.0537	77%(H-9→L)+10%(H-7→L+1)+8%(H-7→L)
6	2.3829	520	0.1335	40%(H-1→L+9)+39%(H-1→L+8)+7%(H-2→L+11)
7	2.3902	519	0.0493	87%(H-8→L+1)
8	2.4108	514	0.3540	24%(H-4→L+3)+12%(H-6→L+1)+8%(H-8→L+1)+6%(H-6→L+2)+6%(H-5→L+1)
9	22.4368	509	1.1080	30%(H-7→L)+13%(H-6→L+1)+10%(H-9→L)+5%(H-7→L+2)
10	2.4836	499	0.0995	63%(H-7→L+2)+8%(H-4→L+3)
11	2.5050	495	0.6234	27%(H-7→L+2)+10%(H-6→L+2)+9%(H-5→L+3)+8%(H-5→L+4)
12	2.5200	492	0.1371	87%(H-11→L)
13	2.5469	487	0.0594	29%(H-3→L+3)+14%(H-3→L+5)+10%(H→L+4)+9%(H-2→L+2)
14	2.5548	485	0.0330	90%(H-5→L+3)
15	2.5823	480	0.0308	74%(H-10→L+1)+18%(H-8→L+2)
16	2.6297	471	0.7761	29%(H-7→L+3)+14%(H-6→L+2)+12%(H-3→L+5)
17	2.6342	471	0.3495	52%(H→L+10)+6%(H-3→L+5)
18	2.6784	463	0.3495	84%(H-1→L+11)
19	2.6893	461	0.1385	34%(H-7→L+3)+12%(H-1→L+11)+10%(H-1→L+9)
20	2.7752	450	0.0956	18%(H-2→L+8)+17%(H-1→L+10)+8%(H-7→L+3)+7%(H-2→L+9)+6%(H-4→L+3)
21	2.8203	440	0.6712	52%(H-3→L+10)+18%(H-3→L+5)
22	2.8930	428	0.0963	92%(H-2→L+12)
23	2.9137	425	1.0219	26%(H-2→L+9)+18%(H-3→L+10)+10%(H-1→L+8)
24	2.9400	422	3.0532	23%(H-3→L+10)+14%(H-3→L+5)+10%(H-5→L+6)+9%(H-2→L+9)
25	2.9858	415	0.6997	40%(H-5→L+4)+40%(H-5→L+6)
26	3.0466	407	0.0847	52%(H-5→L+4)+ 40%(H-5→L+6)
27	3.0536	406	0.0451	84%(H-4→L+8)+12%(H-4→L+9)

**Table S3.** Excitation energy (E), oscillator strength (f) and composition of the lowest singlet excited states (Si) with  $f > 0.02$  for the fishbone 1 aggregate computed at B3LYP(6-31G(d,p)) level of theory –negative charge.

	E (eV)	E (nm)	f	MOs
S <sub>1</sub>	2.2238	557	0.0512	65%(H→L)+19%(H-1→L)+10%(H-2→L)
S <sub>2</sub>	2.2491	551	0.0623	50%(H→L+1)+32%(H-1→L+1)+8%(H-1→L)
S <sub>6</sub>	2.5976	477	0.2100	46%(H→L+3)+26%(H-2→L+3)+9%(H-2→L)
S <sub>8</sub>	2.6485	468	0.1306	65%(H→L+2)+24%(H-3→L+2)
S <sub>9</sub>	2.7118	457	0.1283	52%(H-1→L+2)+29%(H-3→L+2)
S <sub>10</sub>	7292	454	0.1167	34%(H→L+3)+17%(H-1→L+3)+16%(H-2→L)+11%(H-3→L+1)
S <sub>11</sub>	2.7436	452	0.1165	52%(H-1→L+3)+13%(H-2→L)+11%(H-3→L+1)
S <sub>12</sub>	2.8285	438	0.1514	35%(H-3→L+1)+10%(H-1→L+2)
S <sub>13</sub>	2.9536	420	0.4476	72%(H-2→L+2)
S <sub>14</sub>	2.9693	417	0.7401	24%(H-3→L+2)+23%(H-2→L+2)+12%(H→L+3)+16%(H-2→L+3)
S <sub>16</sub>	3.1201	397	2.5358	16%(H-2→L+3)+12%(H-3→L+2)+10%(H-1→L+2)

**Table S4.** Excitation energy (E), oscillator strength (f) and composition of the lowest singlet excited states (Si) with  $f > 0.02$  for the [DAMS<sup>+</sup>] dimer aggregate computed at B3LYP(6-31G(d,p)) level of theory –negative charge.

	E (eV)	E (nm)	f	MOs
S <sub>1</sub>	2.2618	548	0.0638	87%(H→L)+10%(H-1→L)
S <sub>2</sub>	2.5643	483	0.1793	58%(H-1→L)+34%(H→L+1)
S <sub>3</sub>	2.773	446	0.1474	54%(H-1→L)+18%(H→L+1)
S <sub>4</sub>	3.0169	411	1.9670	34%(H-1→L+1)+27%(H→L+1)+11%(H-1→L)

**Table S5.** Excitation energy (E), oscillator strength (f) and composition of the lowest singlet excited states (S<sub>i</sub>) with  $f > 0.02$  for the [DAMS<sup>+</sup>] monomer computed at B3LYP(6-31G(d,p)) level of theory –negative charge.

	E (eV)	E (nm)	f	MOs
S <sub>1</sub>	2.8871	429	1.3026	72%(H→L)

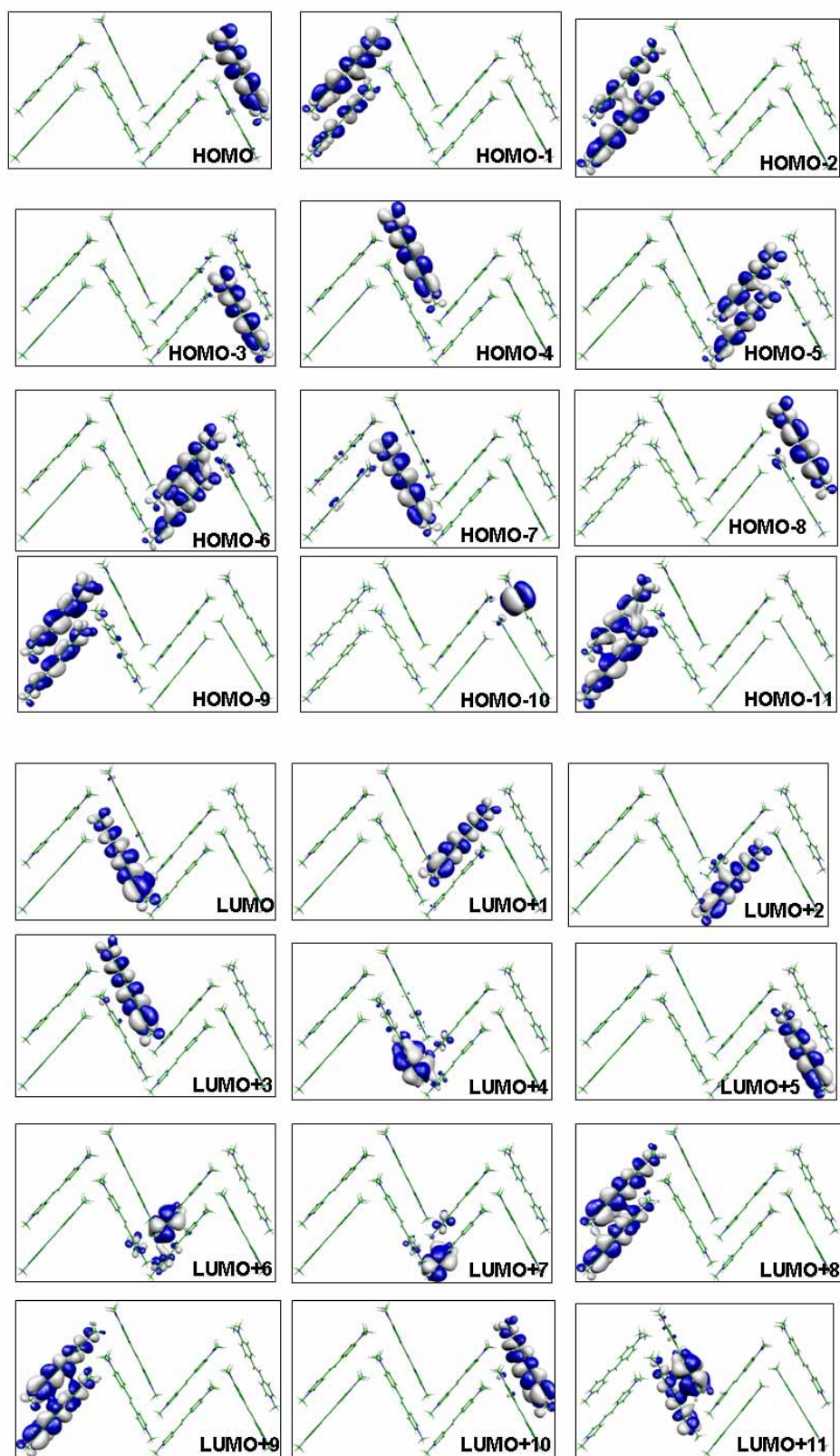
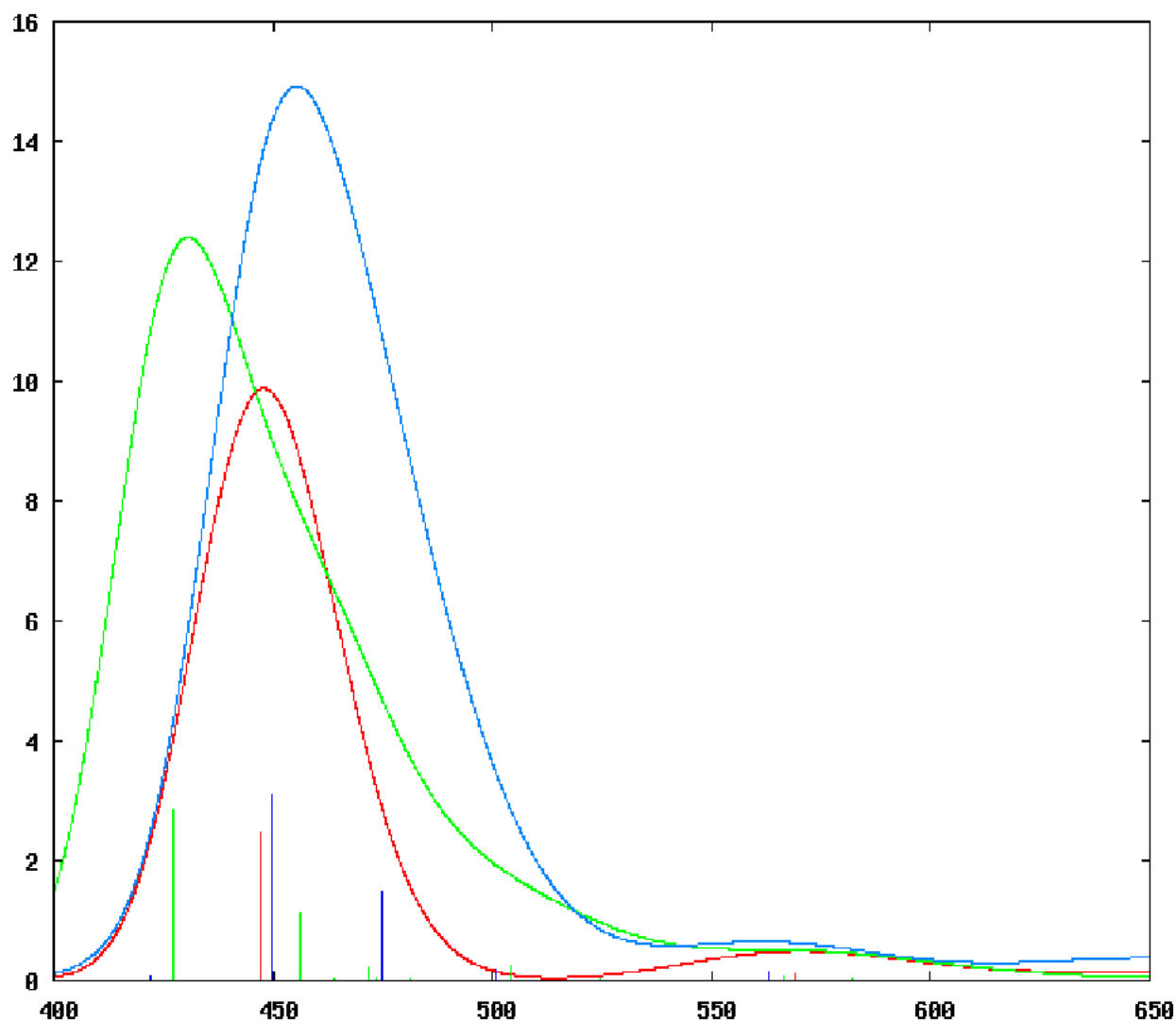
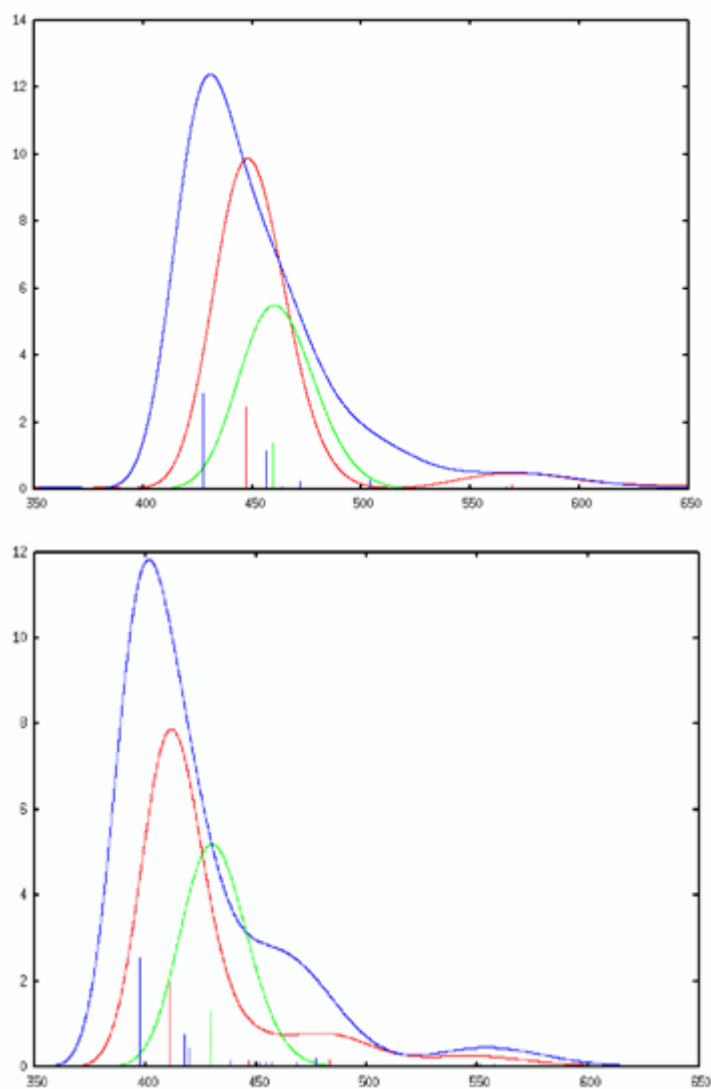


Figure S1: Calculated MOs for the fishbone-like model 2





**Figure S2:** Calculated (B3LYP/6-31G(d,p)) absorption spectra of the slipped dimer (red line), tetrameric model **1** (green line) and the fishbone-like structural motif where four [DAMS<sup>+</sup>] chromophores stacked on two adjacent columns are facing towards the N-methyl groups (blue line).



**Figure S3:** Calculated (B3LYP/6-31G(d,p)) absorption spectra of monomeric [DAMS<sup>+</sup>] (green line), dimeric J-type stacking (red line) and fishbone-like aggregates models 1 (blue line), only cations (top panel) and with negative charges located at the X-ray counteranions position (bottom panel).