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

Supporting Information

for

Theoretical insights into dopamine photochemistry adsorbed on graphene-type nanostructures

by

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	S_1	S_2	S_3	S_4	S_5	S_6	S_7
Energy	2.36	3.79	3.93	5.44	6.19	6.38	6.53
	(526)	(327)	(315)	(228)	(200)	(194)	(190)
Osc. Str.	0.00003	0.00001	0.07752	0.00001	0.00019	0.17737	0.00000
Orb. Trans.	H → L	H – 3 → L	H – 1 → L	H – 2 → L	H → L + 1	H – 4 → L	H → L + 2
	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}
Energy	6.82	6.89	7.12	7.37	7.64	7.77	7.80
	(182)	(180)	(174)	(168)	(162)	(160)	(159)
Osc. Str.	0.02025	0.00012	0.00038	0.27744	0.78035	0.00614	0.06234
Orb. Trans.	H – 2 → L + 3	H – 6 → L	H – 8 → L	H – 1 → L + 1	H – 1 → L + 2	H – 12 → L	H – 7 → L

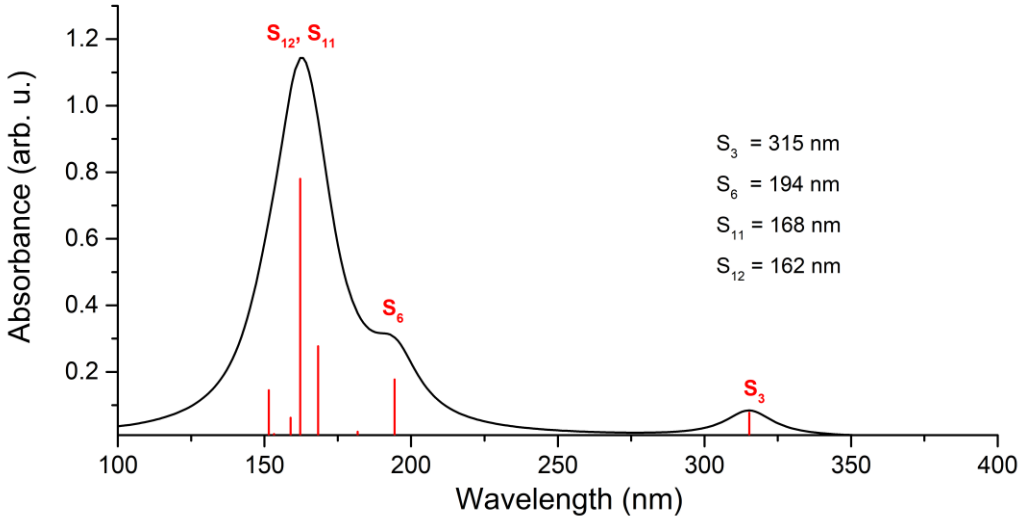
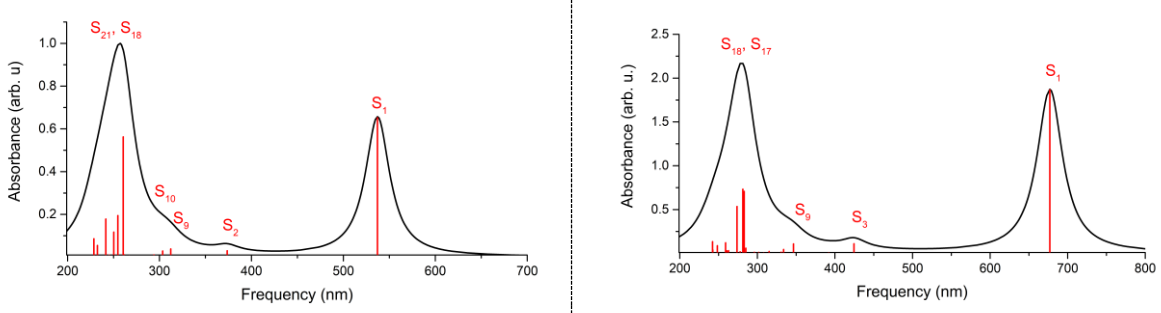


Figure S1. Theoretical UV-absorption spectra for DAQ, computed at TDDFT/ωB97X-D3BJ/def2-TZVPP level of theory.

2. Electronic excited states and theoretical UV-absorption spectra for GrNP- and GrS-type graphene structures



(a) GrNP (with optimized C–C bonds) *(b) GrS (with fixed[1] C–C bonds)*

Figure S2. Theoretical UV-absorption spectra for GrNP- *(a)* and GrS-type *(b)* graphene nanoparticle geometries, computed at TDDFT/ωB97X-D3BJ/def2-TZVPP level of theory.

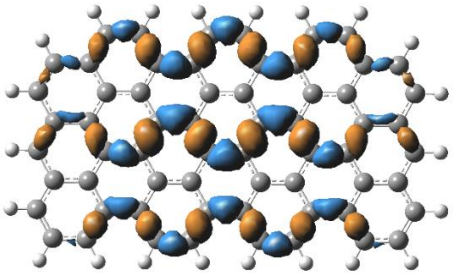
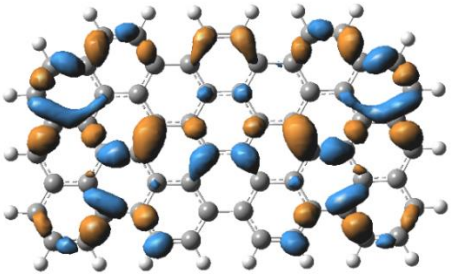
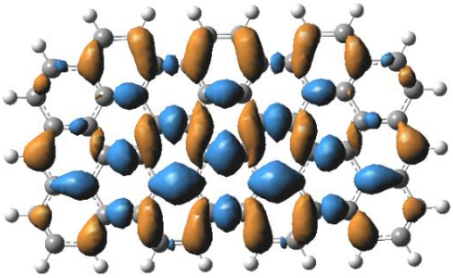
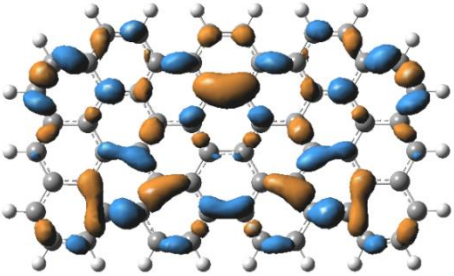
Table S2. The excitation energy, oscillator strength and the largest orbital transition coefficients of the first 30 electronic excited states computed for the GrNP- and GrS-type graphene nanoparticle geometries at TDDFT/ωB97X-D3BJ/def2-TZVPP level of theory (H = HOMO and L = LUMO). The most relevant electronic excited states are marked with red color.

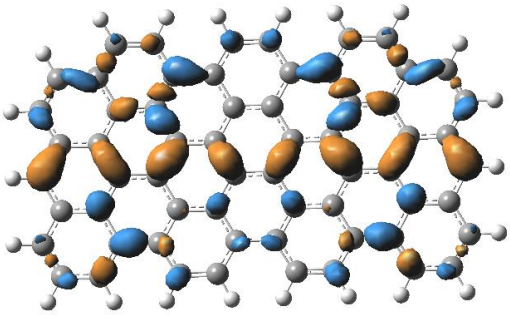
GrNP				GrS			
Nr.	Freq. (nm)	Strength	orb. trans.	Nr.	Freq. (nm)	Strength	orb. trans.
S_1	537.1	1.7945	H → L	S_1	677.0	1.8644	H → L
S_2	373.7	0.0823	H → L+1 H-1 → L	S_2	435.0	0.0007	H → L+2
S_3	373.2	0.0002	H → L+2	S_3	424.7	0.1096	H → L+1
S_4	363.2	0.0009	H-3 → L	S_4	399.9	0.0011	H-3 → L H → L+3
S_5	355.9	0.0000	H → L+3	S_5	399.4	0.0001	H-2 → L
S_6	339.3	0.0017	H → L+5	S_6	391.9	0.0061	H-1 → L
S_7	324.9	0.0006	H-1 → L H → L+1	S_7	366.0	0.0020	H → L+4
S_8	321.6	0.0055	H-2 → L	S_8	364.9	0.0002	H → L+5
S_9	312.3	0.1052	H → L+7	S_9	346.6	0.1074	H → L+6 H → L+7
S_{10}	303.5	0.0790	H-5 → L	S_{10}	333.9	0.0446	H-6 → L
S_{11}	302.7	0.0100	H → L+7 H-2 → L	S_{11}	330.6	0.0131	H → L+7
S_{12}	294.0	0.0282	H-1 → L+5 H → L+8	S_{12}	315.2	0.0218	H-5 → L H → L+8
S_{13}	284.5	0.0150	H → L+9	S_{13}	308.2	0.0051	H → L+9
S_{14}	281.1	0.0032	H-4 → L	S_{14}	301.8	0.0105	H-4 → L
S_{15}	267.2	0.0201	H-6 → L	S_{15}	296.2	0.0115	H → L+8 H-8 → L

[1] The length of each C–C bond was fixed to 1.42 Å.

S_{16}	265.6	0.0041	H-5 → L H-7 → L	S_{16}	285.2	0.0585	H-5 → L H → L+7
S_{17}	261.3	0.0310	H-9 → L	S_{17}	283.2	0.7067	H-3 → L
S_{18}	260.6	1.5476	H → L+4	S_{18}	281.3	0.7330	H-7 → L
S_{19}	258.7	0.0096	H-3 → L+2	S_{19}	277.8	0.0177	H → L+11
S_{20}	257.4	0.0000	H-9 → L	S_{20}	273.8	0.5347	H → L+10
S_{21}	254.8	0.5355	H → L+10	S_{21}	271.5	0.0024	H-9 → L
S_{22}	252.0	0.0046	H-2 → L+3	S_{22}	266.3	0.0001	H-2 → L+4 H → L+13
S_{23}	250.3	0.3219	H → L+11	S_{23}	263.0	0.0302	H-3 → L+2 H-2 → L+3
S_{24}	245.2	0.0256	H-10 → L	S_{24}	260.9	0.0289	H-1 → L+1
S_{25}	241.6	0.4908	H-2→ L+4	S_{25}	259.1	0.1202	H-10 → L
S_{26}	238.4	0.0014	H-2 → L+5	S_{26}	258.6	0.0000	H-7 → L H → L+9
S_{27}	232.5	0.1506	H-1 → L+4	S_{27}	250.2	0.0052	H-10 → L H-2 → L+5
S_{28}	232.3	0.0022	H-1 → L+2 H-2 → L+1	S_{28}	248.5	0.0873	H-1 → L+4
S_{29}	229.3	0.0204	H-1 → L+3	S_{29}	242.6	0.0393	H-1 → L+4
S_{30}	228.7	0.2366	H-3 → L+1 H-1 → L+4	S_{30}	242.2	0.1338	H-1 → L+5

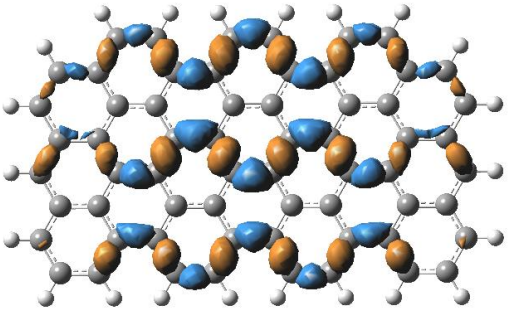
Table S3. The natural difference orbitals (NDO) between the ground and the given electronic excited state computed for the the GrNP- and GrS-type graphene geometries at TDDFT/ωB97X-D3BJ/def2-TZVPP level of theory.

GrNP:	
	
S_1	S_2
	
S_9	S_{10}

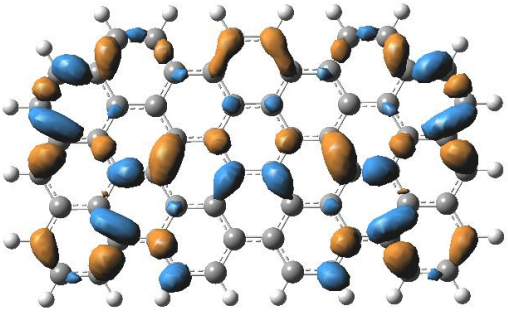


S_{18}

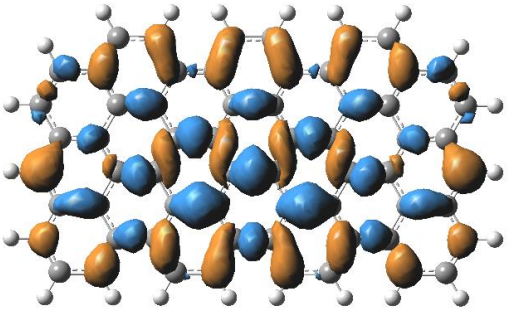
GrS:



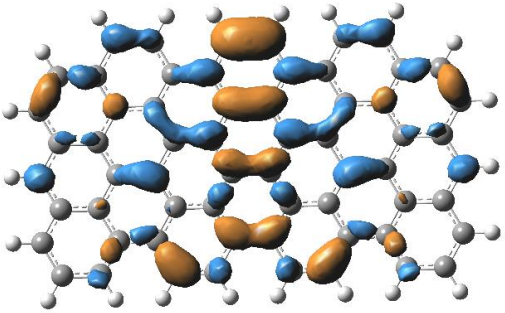
S_1



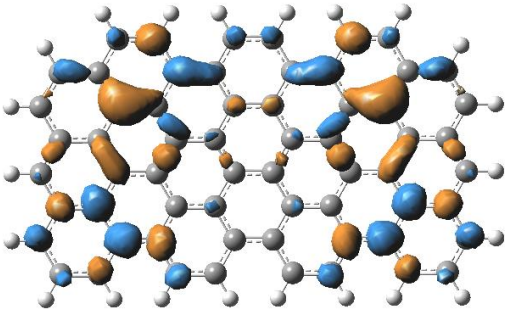
S_3



S_9



S_{17}



S_{18}

3. Electronic excited states and theoretical UV-absorption spectra for GrNP – DA binary complex.

Table S4. The frontier (HOMO and LUMO) orbitals of the isolated DA computed at ωB97X-D3BJ/def2-TZVPP level of theory.

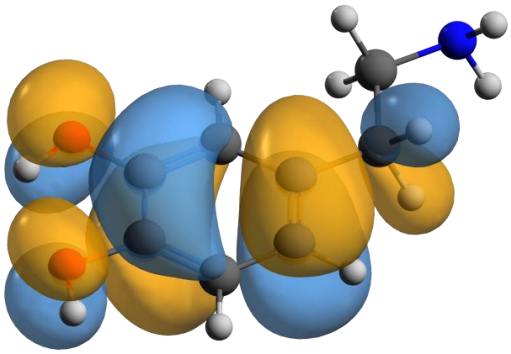
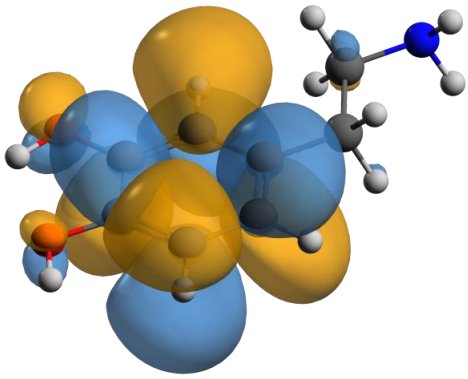
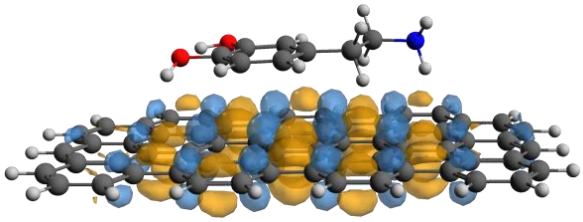
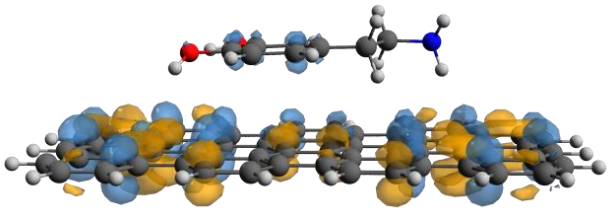
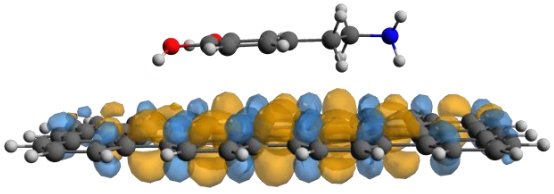
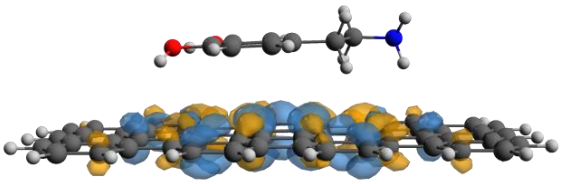
	
HOMO	LUMO

Table S5. The natural difference orbitals (NDO) between the ground and the given electronic excited state computed for the GrNP-DA binary complex at TDDFT/ωB97X-D3BJ/def2-TZVPP level of theory (Blue = hole, Yellow = electron, orbital orders with red text color are specific to DA and blacks are graphene-types).

	
$S_0 \rightarrow S_1$ H → L (91%)	$S_0 \rightarrow S_2$ H – 1 → L (40%) H → L + 1 (42%)
	
$S_0 \rightarrow S_3$ H → L + 2 (53%) H – 3 → L (28%)	$S_0 \rightarrow S_4$ H – 4 → L (40%) H → L + 4 (35%)

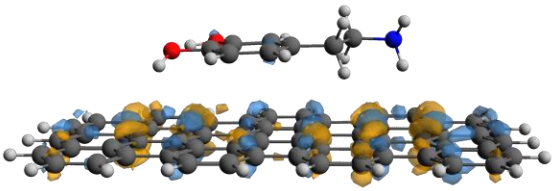
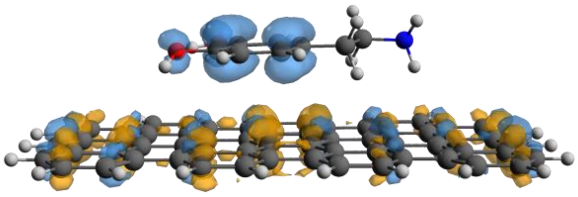
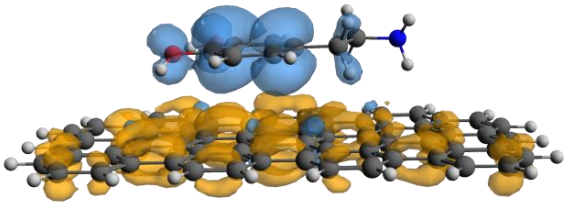
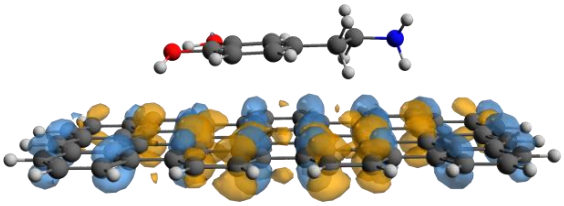
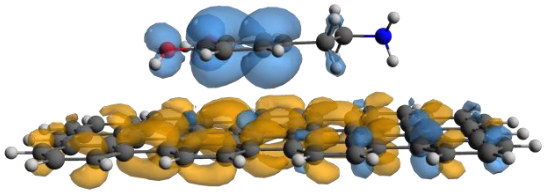
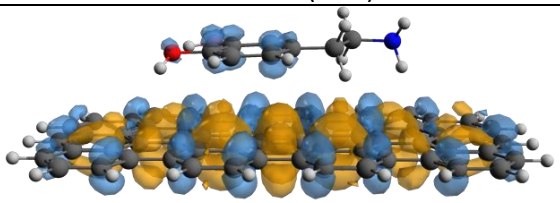
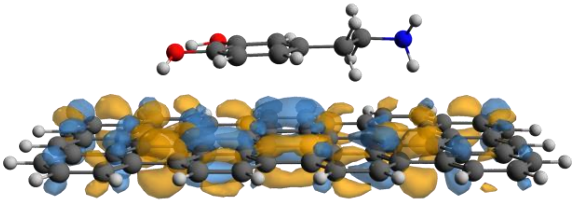
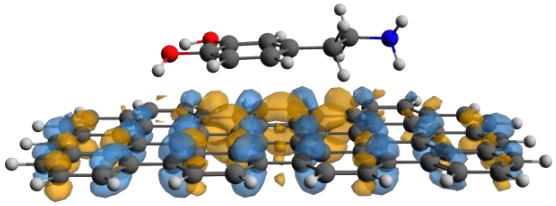
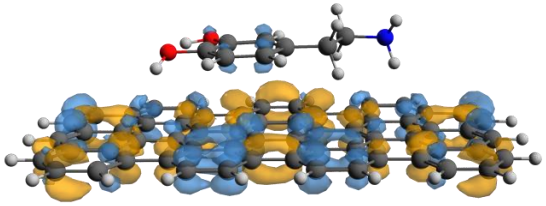
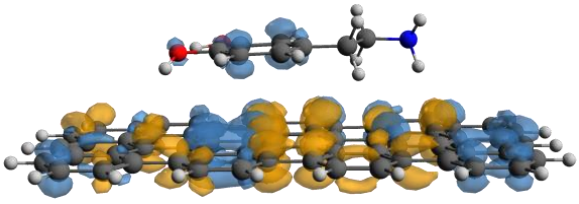
	
$S_0 \rightarrow S_5$ H → L + 3 (40%) H – 5 → L (17%)	$S_0 \rightarrow S_6$ H → L + 5 (37%) H – 1 → L (17%)
	
$S_0 \rightarrow S_7$ H – 2 → L (26%) H → L + 5 (21%)	$S_0 \rightarrow S_8$ H – 3 → L (22%) H → L + 2 (17%)
	
$S_0 \rightarrow S_9$ H – 2 → L (43%)	$S_0 \rightarrow S_{10}$ H → L + 7 (43%); H → L + 6 (21%)
	
$S_0 \rightarrow S_{11}$ H – 7 → L (18%) H → L + 9 (17%)	$S_0 \rightarrow S_{12}$ H → L + 7 (18%)
	
$S_0 \rightarrow S_{13}$ H → L + 8 (23%) H – 1 → L +1 (17%)	$S_0 \rightarrow S_{14}$ H → L + 9 (21%)

Table S5 (cont.). The natural difference orbitals (NDO) between the ground and the given electronic excited state computed for the GrNP-DA binary complex at TDDFT/ωB97X-D3BJ/def2-TZVPP level of theory (Blue = hole, Yellow = electron, orbital orders with red text color are specific to DA and blacks are graphene-types).

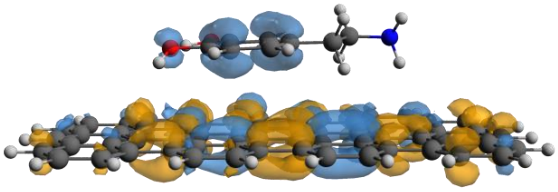
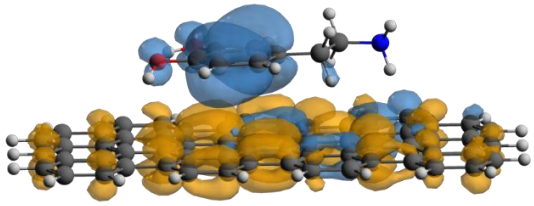
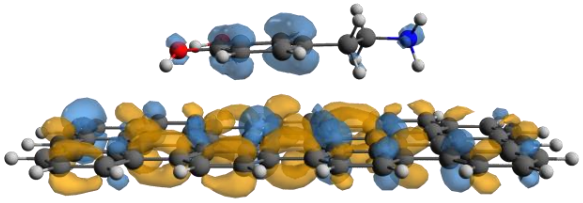
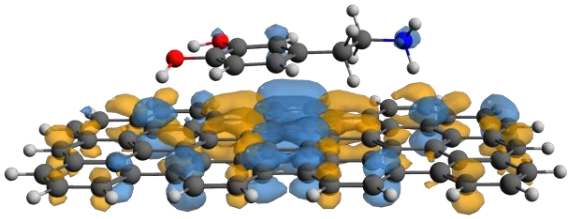
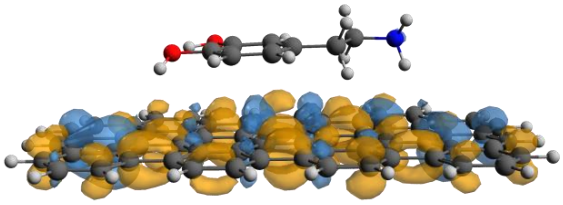
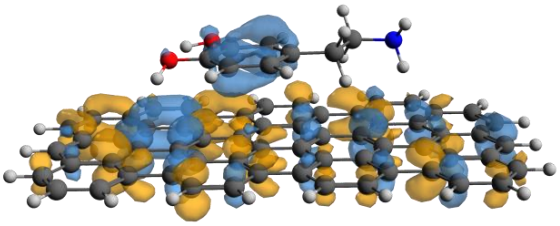
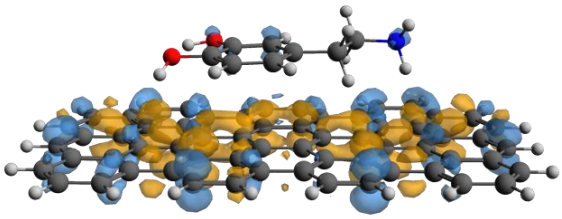
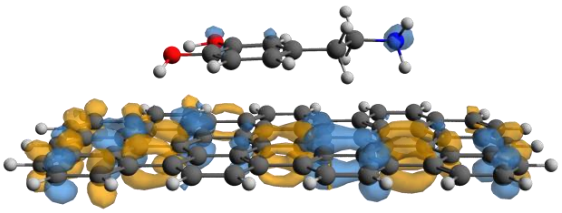
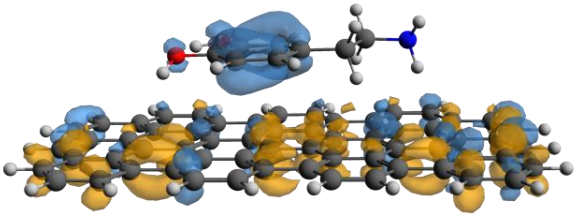
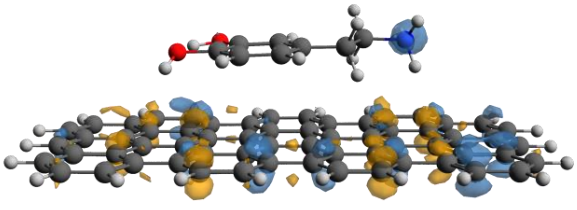
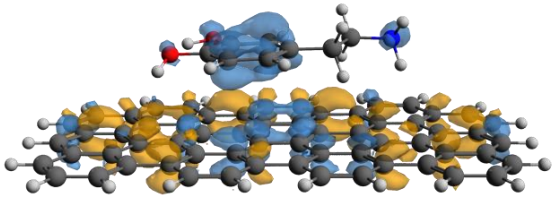
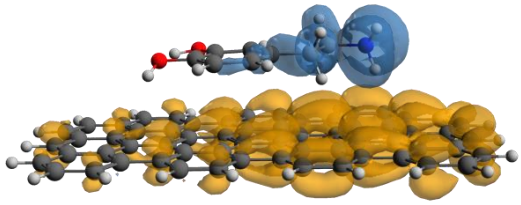
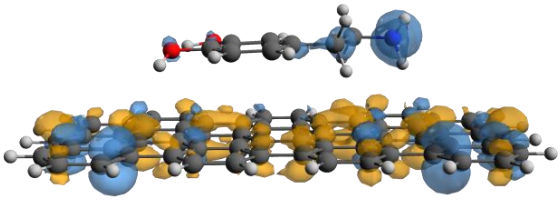
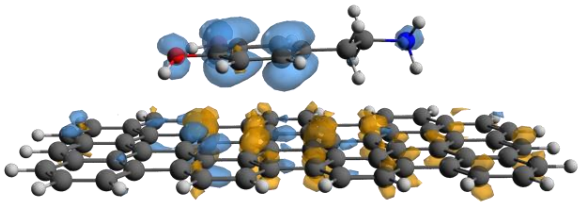
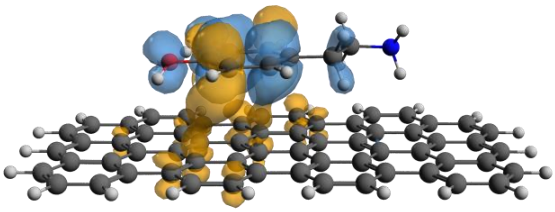
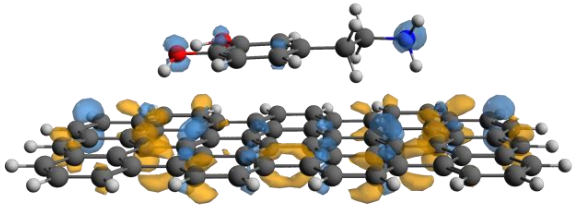
 $S_0 \rightarrow S_{15}$ H – 5 → L (23%)	 $S_0 \rightarrow S_{16}$ H – 6 → L (41%)
 $S_0 \rightarrow S_{17}$ H – 8 → L (26%)	 $S_0 \rightarrow S_{18}$ H – 10 → L (19%)
 $S_0 \rightarrow S_{19}$ H – 12 → L (22%) H – 11 → L (18%)	 $S_0 \rightarrow S_{20}$ H → L + 4 (15%)
 $S_0 \rightarrow S_{21}$ H – 1 → L + 7 (14%); H → L + 11 (13%)	 $S_0 \rightarrow S_{22}$ H – 12 → L (15%)
 $S_0 \rightarrow S_{23}$ H → L + 10 (18%)	 $S_0 \rightarrow S_{24}$ H – 3 → L + 3 (14%)

Table S5 (cont.). The natural difference orbitals (NDO) between the ground and the given electronic excited state computed for the GrNP-DA binary complex at TDDFT/ωB97X-D3BJ/def2-TZVPP level of theory (Blue = hole, Yellow = electron, orbital orders with red text color are specific to DA and blacks are graphene-types).

	
$S_0 \rightarrow S_{25}$ H → L + 11 (10%)	$S_0 \rightarrow S_{26}$ H – 9 → L (60%)
	
$S_0 \rightarrow S_{27}$ H – 13 → L (17%)	$S_0 \rightarrow S_{28}$ H – 1 → L + 1 (24%); H – 3 → L + 3 (20%)
	
$S_0 \rightarrow S_{29}$ H – 2 → L + 12 (26%)	$S_0 \rightarrow S_{30}$ H – 3 → L + 5 (10%)

4. Electronic excited states and theoretical UV-absorption spectra for GrNP – DAQ binary complex.

Table S6. The frontier (HOMO and LUMO) orbitals of the isolated DAQ computed at ωB97X-D3BJ/def2-TZVPP level of theory.

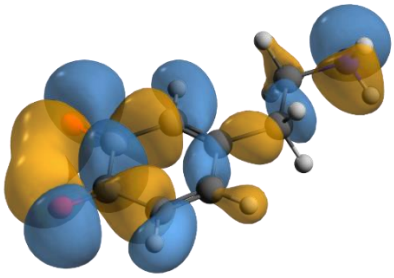
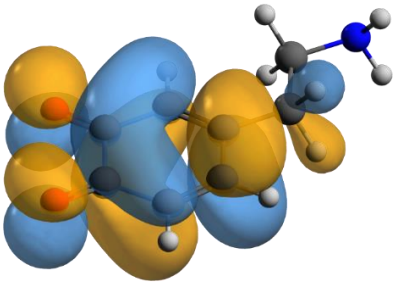
	
HOMO	LUMO

Table S7. The natural difference orbitals (NDO) between the ground and the given electronic excited state computed for the GrNP-DAQ binary complex at TDDFT/ωB97X-D3BJ/def2-TZVPP level of theory (Blue = hole, Yellow = electron, orbital orders with red text color are specific to DA and blacks are graphene-types).

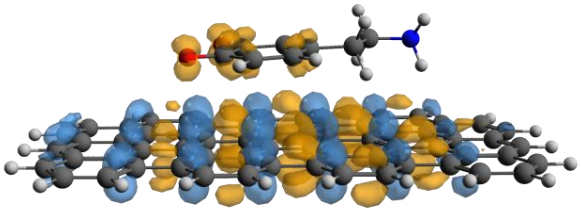
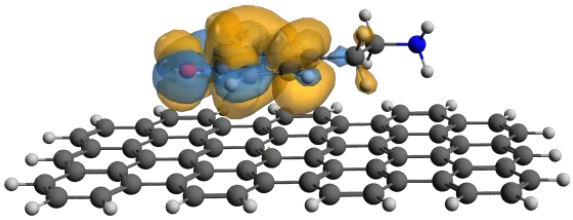
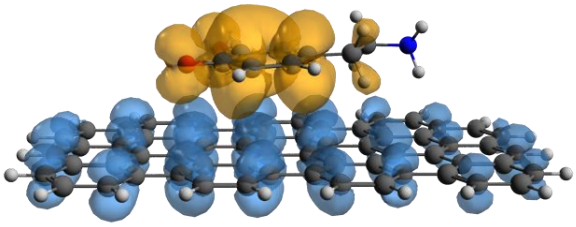
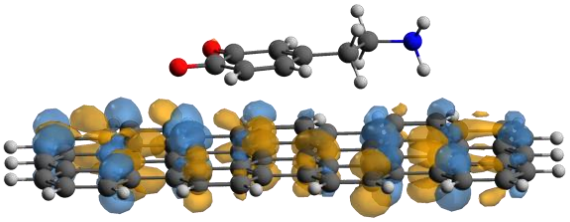
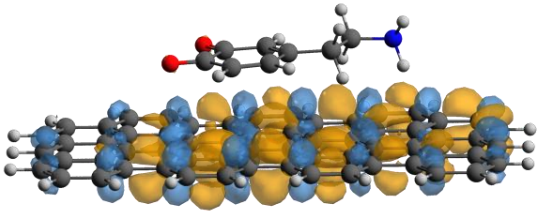
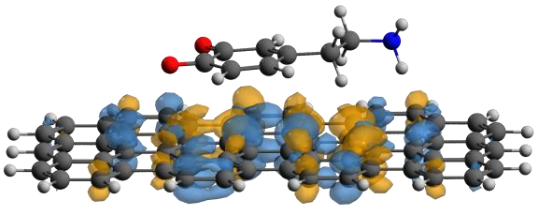
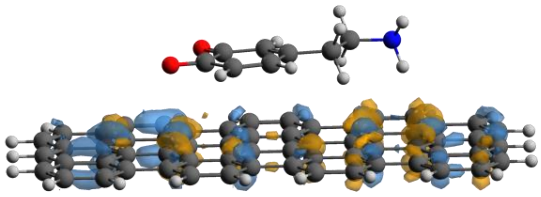
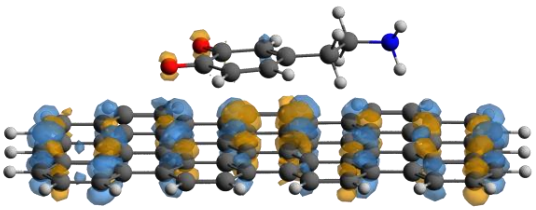
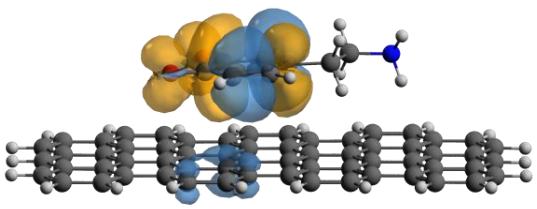
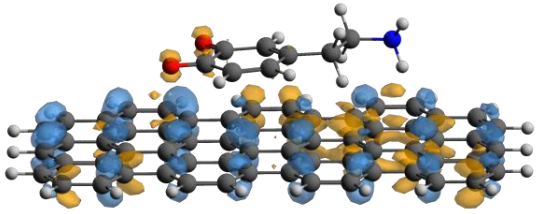
	
$S_0 \rightarrow S_1$ H → L (90%)	$S_0 \rightarrow S_2$ H – 8 → L + 1 (54%); H – 9→ L + 1 (15%)
	
$S_0 \rightarrow S_3$ H → L + 1 (93%)	$S_0 \rightarrow S_4$ H – 1 → L (36%); H → L + 2 (36%)
	
$S_0 \rightarrow S_5$ H → L + 3 (50%); H – 2 → L (28%)	$S_0 \rightarrow S_6$ H – 3 → L (30%); H → L + 4 (36%)
	
$S_0 \rightarrow S_7$ H → L + 4 (17%); H – 2 → L (16%)	$S_0 \rightarrow S_8$ H → L + 5 (19%); H → L + 6 (19%)
	
$S_0 \rightarrow S_9$ H – 7→ L + 1 (26%); H – 9 → L + 1 (28%)	$S_0 \rightarrow S_{10}$ H – 1 → L (32%); H → L + 2 (30%)

Table S7 (cont.). The natural difference orbitals (NDO) between the ground and the given electronic excited state computed for the GrNP-DAQ binary complex at TDDFT/ωB97X-D3BJ/def2-TZVPP level of theory (Blue = hole, Yellow = electron, orbital orders with red text color are specific to DA and blacks are graphene-types).

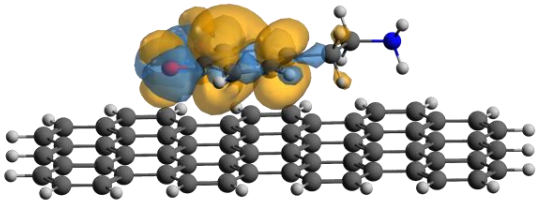
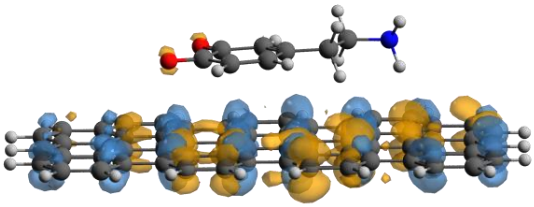
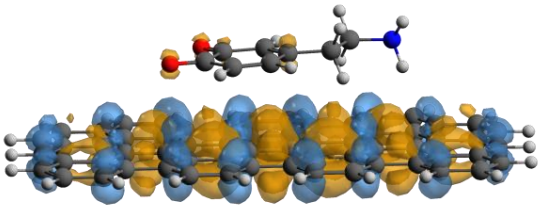
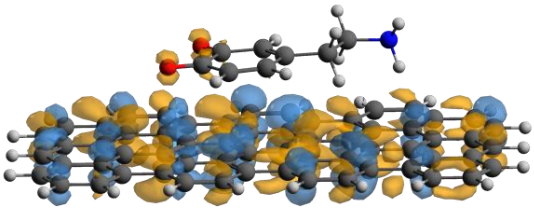
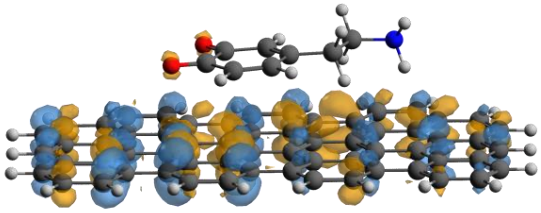
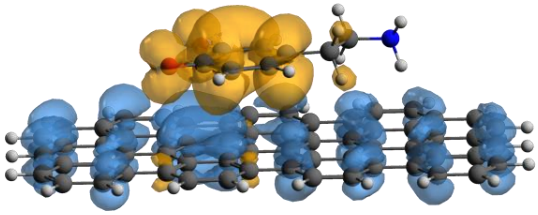
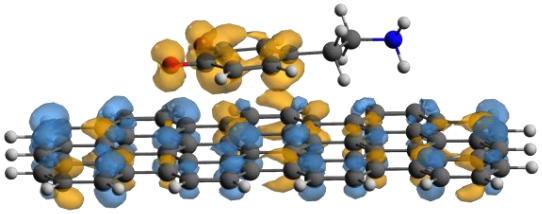
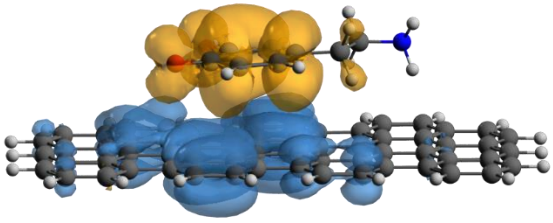
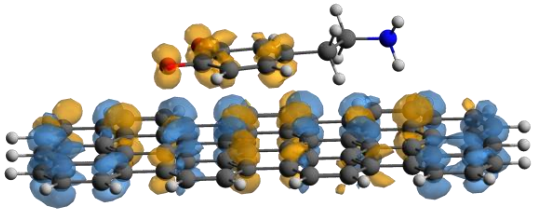
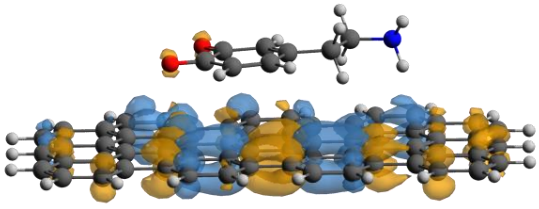
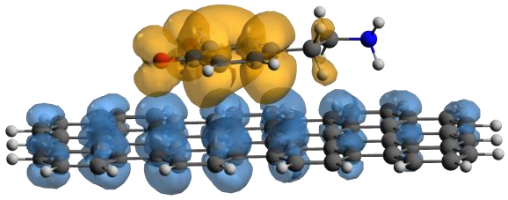
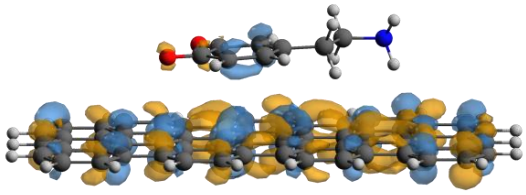
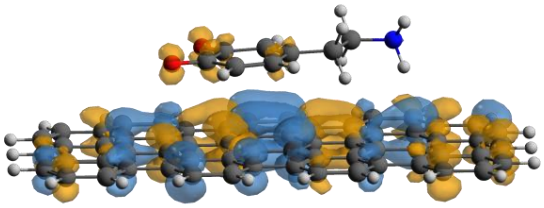
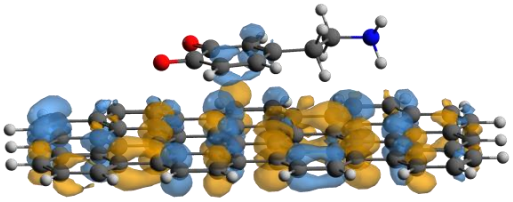
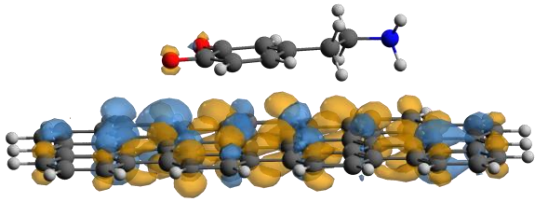
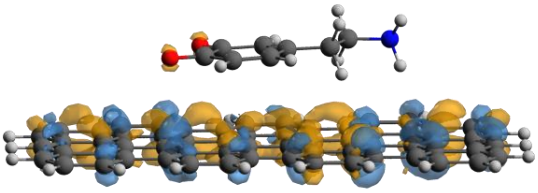
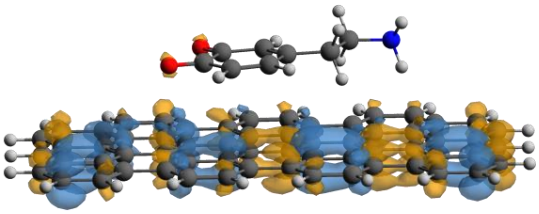
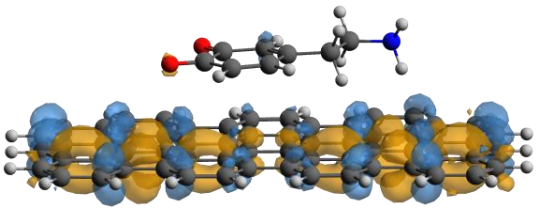
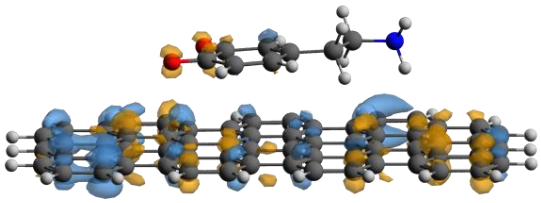
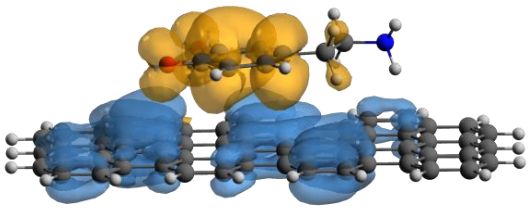
	
$S_0 \rightarrow S_{11}$ H – 19 → L + 1 (63%)	$S_0 \rightarrow S_{12}$ H – 2 → L (24%); H → L + 3 (17%)
	
$S_0 \rightarrow S_{13}$ H → L + 7 (33%); H → L + 8 (34%)	$S_0 \rightarrow S_{14}$ H – 5 → L (13%)
	
$S_0 \rightarrow S_{15}$ H → L + 8 (26%)	$S_0 \rightarrow S_{16}$ H – 1 → L + 1 (64%)
	
$S_0 \rightarrow S_{17}$ H → L + 9 (22%); H – 1 → L + 2 (17%)	$S_0 \rightarrow S_{18}$ H – 3 → L + 1 (61%)
	
$S_0 \rightarrow S_{19}$ H → L + 10 (27%)	$S_0 \rightarrow S_{20}$ H – 4 → L (26%)

Table S7 (cont.). The natural difference orbitals (NDO) between the ground and the given electronic excited state computed for the GrNP-DAQ binary complex at TDDFT/ωB97X-D3BJ/def2-TZVPP level of theory (Blue = hole, Yellow = electron, orbital orders with red text color are specific to DA and blacks are graphene-types).

	
$S_0 \rightarrow S_{21}$ H – 2 → L + 1 (77%); H – 2 → L (28%)	$S_0 \rightarrow S_{22}$ H – 5 → L (17%); H → L + 9 (13%)
	
$S_0 \rightarrow S_{23}$ H – 6 → L (12%)	$S_0 \rightarrow S_{24}$ H – 3 → L (15%); H – 7 → L (12%)
	
$S_0 \rightarrow S_{25}$ H – 12 → L (11%)	$S_0 \rightarrow S_{26}$ H – 3 → L + 3 (10%)
	
$S_0 \rightarrow S_{27}$ H – 11 → L (21%)	$S_0 \rightarrow S_{28}$ H – 1 → L + 7 (17%)
	
$S_0 \rightarrow S_{29}$ H – 4 → L + 4 (8%)	$S_0 \rightarrow S_{30}$ H – 4 → L + 1 (50%); H – 5 → L + 1 (19%)