Polydopamine photochemical behavior under UV irradiation

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Dopamine photochemistry

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Article

Dopamine Photochemical Behaviour under UV Irradiation

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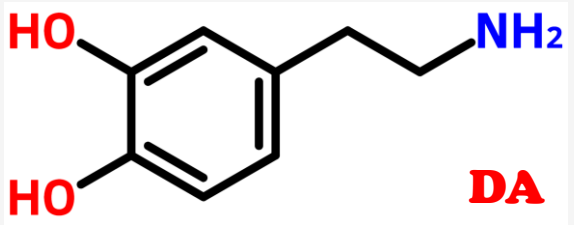
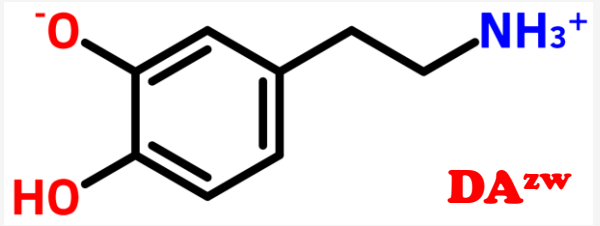
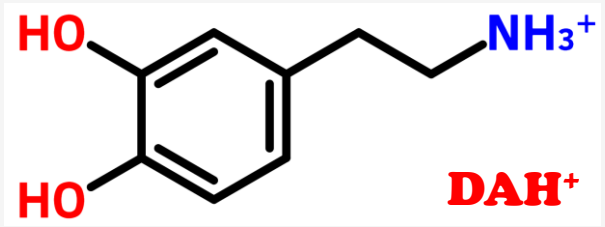


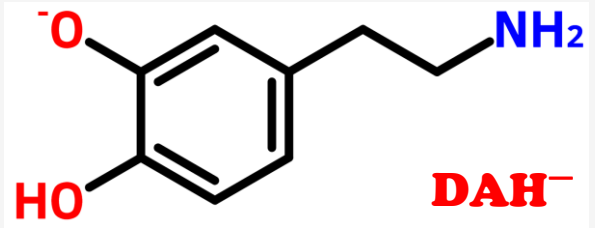


Experimental and theoretical investigation:

DA, DA^{zw}, DAH^{+}, and DAH^{-}

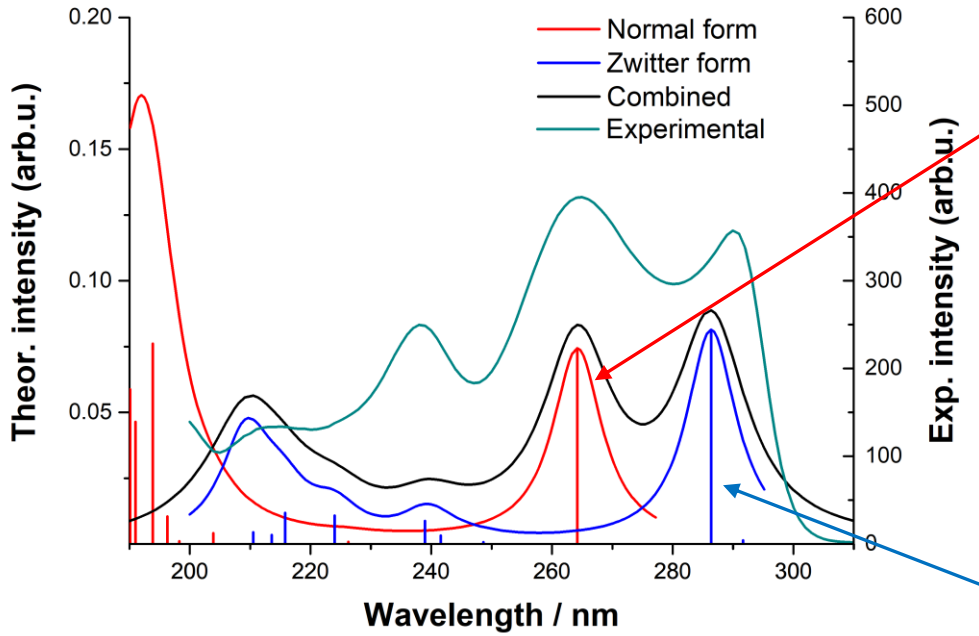


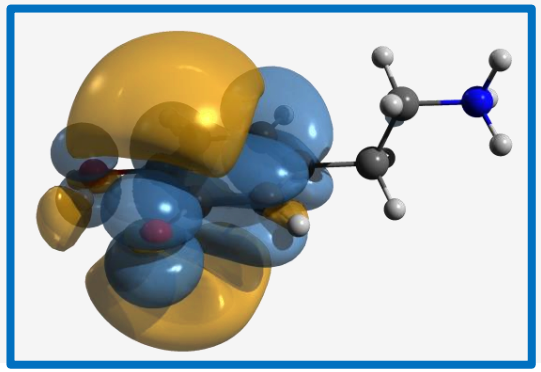
- UV-absorption and Fluorescence emission spectra;
- Fluorescence Lifetimes and Quantum Yield;



Dopamine photochemistry

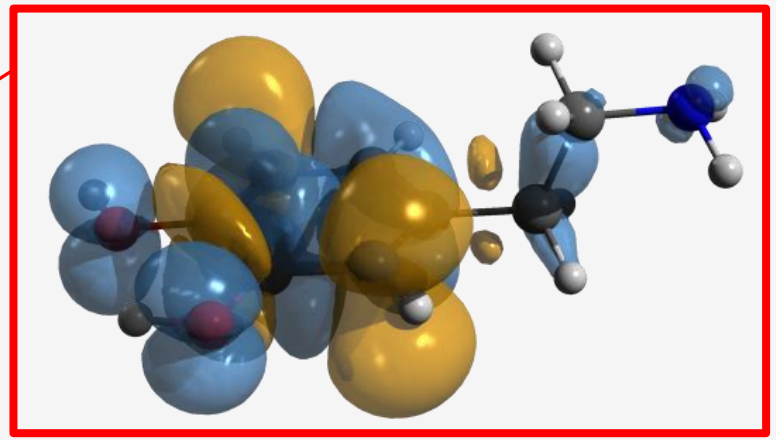
UV-absorption spectra:





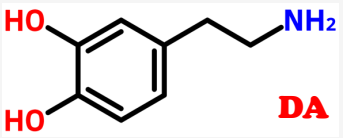
$S_0 \rightarrow S_1$

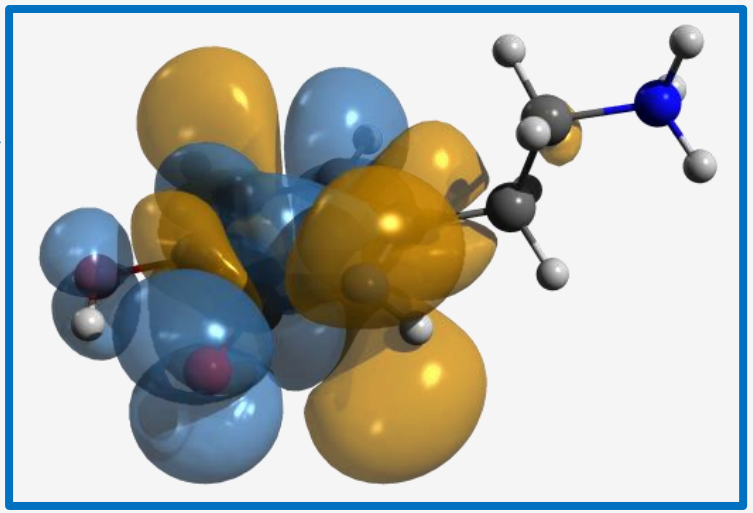
Rydberg state !!!

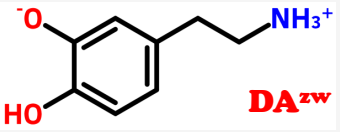


$S_0 \rightarrow S_1$

$n \rightarrow \pi$







$S_0 \rightarrow S_2$

$n \rightarrow \pi$

Dopamine photochemistry

Electronic excited states:

Table 1. Vertical electronic transitions (in nm) and their oscillator strengths in the spectral range of 200–300 nm found for the DA, DA^{zw}, DAH^+, and DAH^- equilibrium geometries obtained at the DLPNO-STEOM-CCSD/ma-def2-TZVPP level of theory.

State	Geometries							
	DA		DA^{zw}		DAH^+		DAH^-	
	ω	f	ω	f	ω	f	ω	f
S_1	266	0.0275	292	0.0014	270	0.0379	302	0.0009
S_2	226	0.0024	286	0.0803	222	0.0011	287	0.0858
S_3	208	0.0637	249	0.0008	209	0.0378	255	0.0033
S_4			242	0.0033			250	0.0164
S_5			239	0.0088			230	0.0947
S_6			224	0.0108			226	0.1094
S_7			216	0.0119			219	0.0050
S_8			214	0.0034			216	0.0018
S_9			211	0.0045			216	0.0107
S_{10}			209	0.0351			211	0.0002

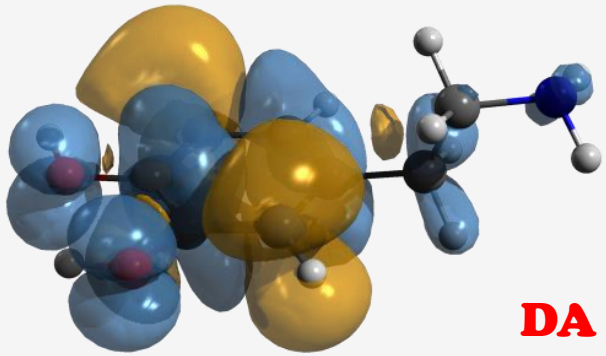
Small oscillator strength (***f***) for S_1 state in case of **DA^{zw}** and **DAH^-**

Dopamine photochemistry

Absorption - Emission:

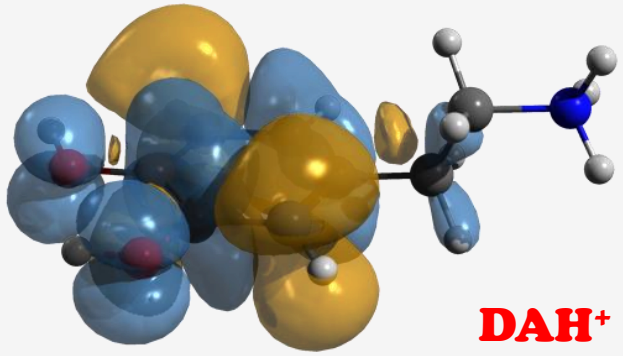
$S_1 \rightarrow S_0$

	DA		DA^{zw}		DAH^+		DAH^-	
	λ^{abs}	λ^{em}	λ^{abs}	λ^{em}	λ^{abs}	λ^{em}	λ^{abs}	λ^{em}
ωB97X-D3	240.3	269.9	274.3	317.2	239.4	268.9	282.7	323.8
DLPNO-STEOM-CCSD	265.5	301.4	291.7 (286.4)	334.3	269.7	299.6	302.2 (286.8)	340.1
Exp.	280	317	280	317	280	317	280	317

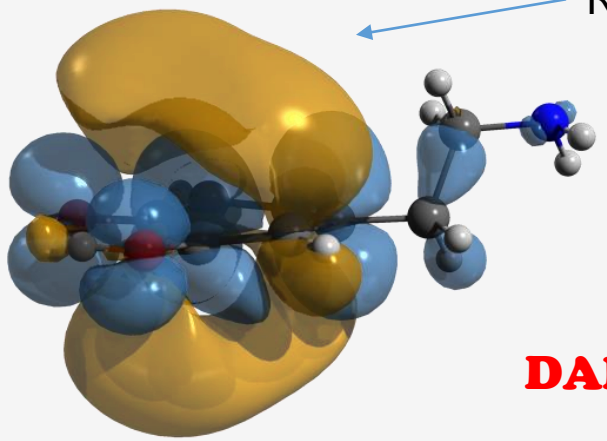


DA

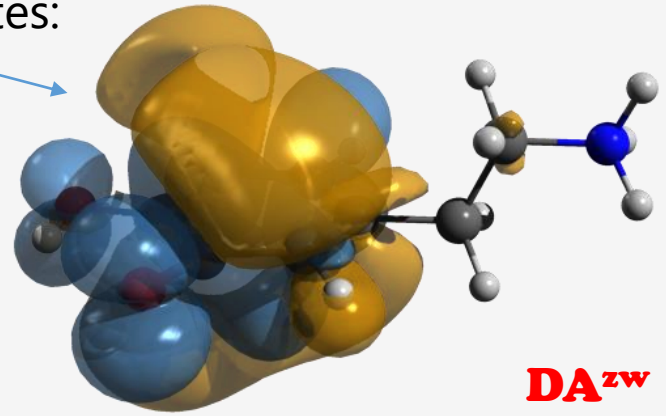
Rydberg states:



DAH^+



DAH^-



DA^{zw}

Dopamine photochemistry

Excited state lifetime (experimental):

Table 2. The parameter fits (fluorescence lifetime components, errors, relative amplitude, and amplitude average lifetime) calculated using the reconvolution method for the concentrated, respectively diluted, solutions at both pH values.

pH	Solution	Reconv. Method	τ_1 (ns)	Error	Ampl. (%)	τ_2 (ns)	Error	Ampl. (%)	$\tau_{avr.}$ (ns)	Error
5.5	Concentrated	1-exp	0.89	0.01	100	-	-	-	-	-
		2-exp	0.91	0.02	99.58	4.86	0.38	0.42	0.99	0.03
	Diluted	1-exp	0.93	0.07	100	-	-	-	-	-
8.0	Concentrated	2-exp	0.89	0.01	95.83	2.98	0.20	4.17	0.97	0.05
	Diluted	2-exp	0.71	0.10	88.97	3.23	0.24	11.03	1.56	0.15
9.0	Concentrated	2-exp	0.69	0.02	92.61	2.41	0.20	7.40	0.82	0.01
	Diluted	2-exp	0.64	0.10	88.20	2.96	0.18	11.80	0.91	0.11

Dopamine photochemistry

Excited state lifetime (theoretical):

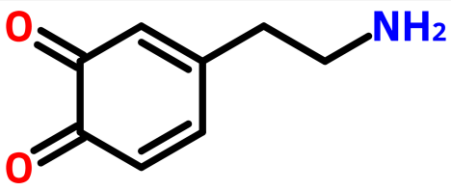
	DA	DA^{zw}	DAH^{+}	DAH^{-}
FC [a]	4.39×10^{-9} (100%)	8.47×10^{-7} (100%)	4.70×10^{-9} (100%)	1.36×10^{-6} (100%)
FC+HT [b]	3.79×10^{-9} (86%, 14%)	2.75×10^{-9} (0%, 100%)	4.51×10^{-9} (96%, 4%)	1.14×10^{-8} (1%, 99%)
FC+(HT+D [c])	3.16×10^{-9} (81%, 19%)	1.02×10^{-9} (0%, 100%)	2.95×10^{-9} (78%, 22%)	7.10×10^{-9} (0%, 100%)

[a] Franck–Condon approximation. [b] Herzberg-Teller approximation. [c] Duschinsky rotation effects.

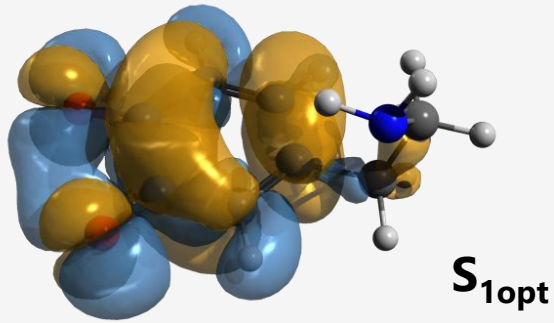
pH	Solution	QY (%)
5.5	Concentrated	3.4
	Diluted	3.4
8.0	Concentrated	2.0
	Diluted	2.4

Quantum Yield

Photochemistry of polydopamine constituents



Dopamine o-quinone



Electronic excited states:

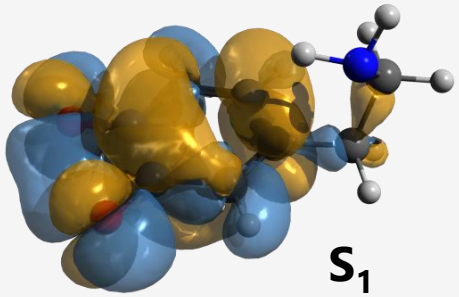
	ωB97X-D3	DLPNO-STEOM-CCSD
S_1	512.3	581.3
S_2	366.2	375.0
S_3	322.9	349.2
S_4	277.4	248.8
S_5	213.5	213.8

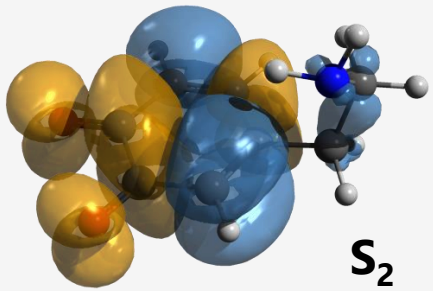
Fluorescence emission:

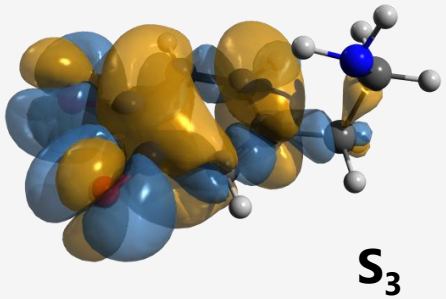
	ωB97X-D3	f
S_1	607.6	0.0003
S_2	403.1	0.1112

Fluorescence lifetime:

τ = 3.55 µs







Photochemistry of polydopamine polymer (trimer) chains

Excited state geometry optimization with DFT – Problems with the exchange correlation functionals

They were optimized for ground electronic states !!!

Lack of electron – hole interaction (charge transfer effects)

Reference method: EOM-CCSD/def2-TZVP(-f)

	Δ(C-C arom)	Δ(C-O)	Δ(C-C)	Δ(C-C alif)	Δ(C-N)	Total
ωB97X	0.00617	0.00525	0.00370	0.00090	0.00780	0.0048
ωB97X-D3	0.00628	0.00605	0.00440	0.00140	0.00830	0.0053
ωB97X-D3BJ	0.00470	0.00090	0.00110	0.00150	0.00230	**0.0021**
ωB97X-V	**0.00365**	0.00040	0.00240	**0.00460**	0.00150	**0.0025**

Values are given in Å

ωB97X-D3BJ can reproduce quite well the EOM-CCSD results !!!

Photochemistry of polydopamine polymer (trimer) chains

How accurate can DFT functionals reproduce the STEOM-DLPNO-CCSD results of excited state energies?

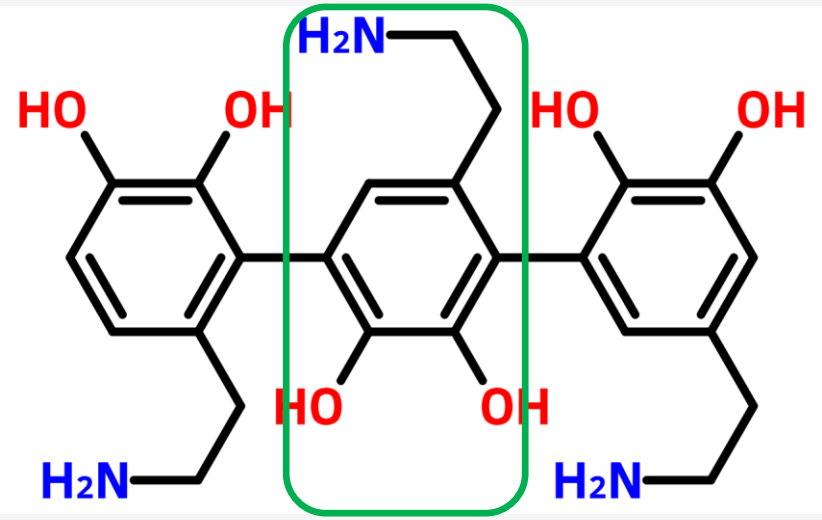
	ΔS_1 (nm)	ΔS_2 (nm)	ΔS_3 (nm)	ΔS_4 (nm)	Average (nm)
B3LYP-D3BJ	11.0	-27.0	-23.0	-23.0	21
CAM-B3LYP-D3	21.0	-7.0	-1.0	-6.0	8.75
revPBE0-D3	16.0	-17.0	-14.0	-16.0	15.75
MN15	19.0	14.0	-2.0	9.0	11
TPSS-D3	**-5.0**	-38.0	-42.0	-50.0	33.75
TPSSh_05-D3	3.0	-31.0	-33.0	-39.0	26.5
TPPSh_10-D3	8.0	-25.0	-26.0	-29.0	22
TPPSh_20-D3	16.0	-14.0	-13.0	-16.0	14.75
TPPSh_25-D3	20.0	-9.0	-7.0	-12.0	12
ωB97X-D3	24.0	8.0	2.0	6.0	10
ωB97X-D3BJ	26.0	7.0	3.0	6.0	10.5
ωB97X-D4	26.0	7.0	3.0	6.0	10.5
mPW2PLYP	14.0	-21.0	-9.0	-15.0	14.75
PBE-QIDH	20.0	4.0	4.0	2.0	7.5
wB2PLYP	23.0	1.0	4.0	4.0	8
RSX-QIDH	28.0	14.0	7.0	13.0	15.5
wB97X-2	**-20.0**	-17.0	-4.0	-6.0	11.75
SCS-PBE-QIDH	7.7	3.1	0.5	1.3	3.15
SOS-PBE-QIDH	4.5	3.6	-0.5	1.8	2.6

Reference method: DLPNO-STEOM-CCSD/ma-def2-TZVPP

Geometry optimization: with **ωB97X-D3BJ**

Excited state energies: with **SOS-PBE-QIDH**

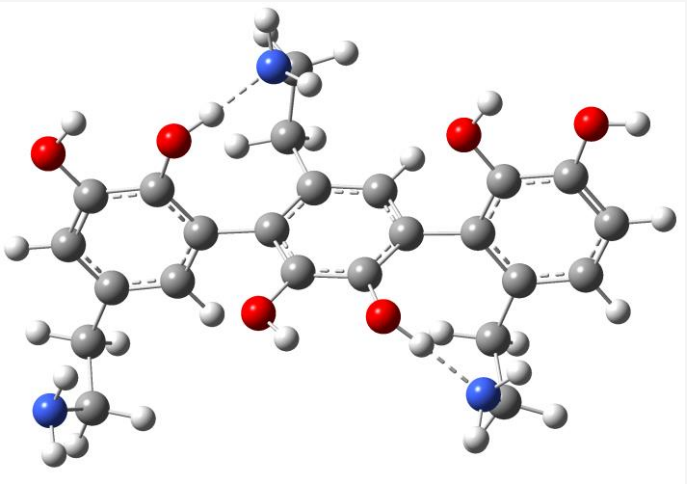
Photochemistry of polydopamine polymer (trimer) chains

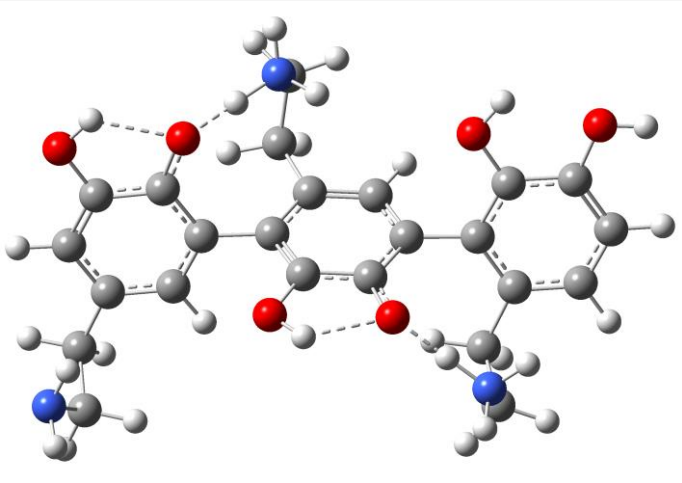


DA-DA-DA

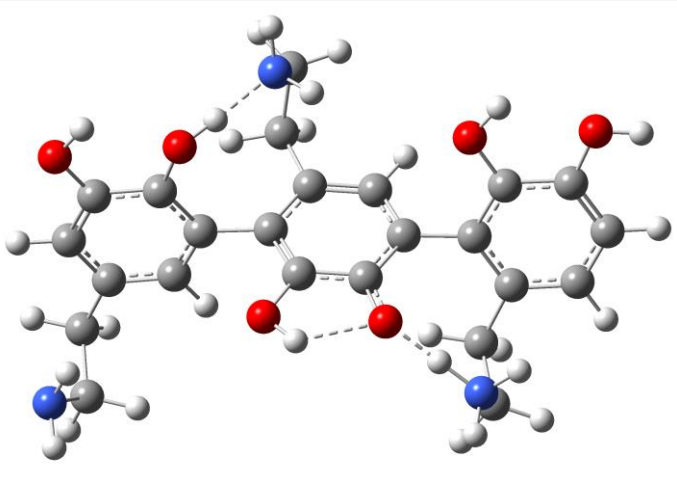
DA-DA^{zw}-DA

DA-DA^{zw}-DA^{zw}





2.64 kcal/mol

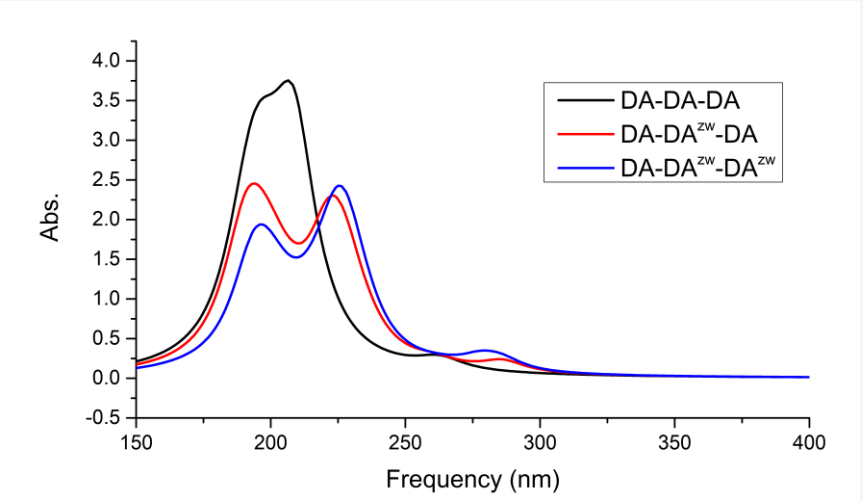


2.37 kcal/mol

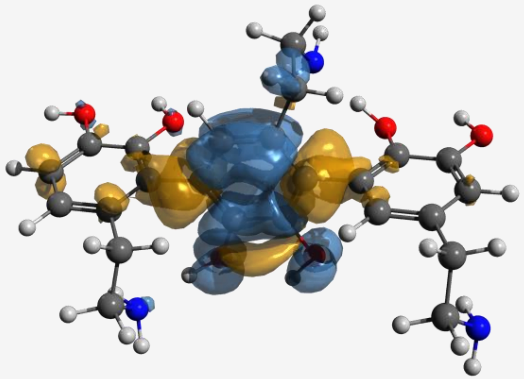
Photochemistry of polydopamine polymer (trimer) chains

Electronic excited states (SOS-PBE-QIDH/ma-def2-TZVPP)

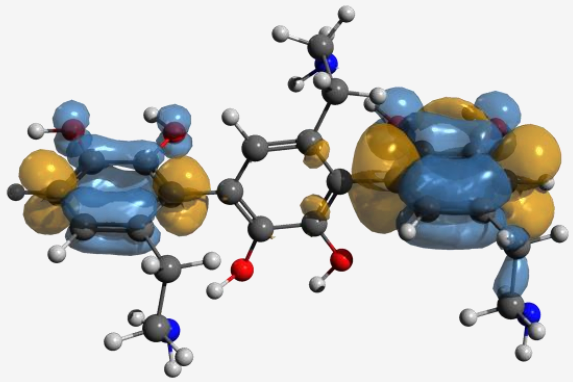
	DA (nm)	DA^{zw} (nm)	DA-DA-DA (nm)	DA-DA^{zw}-DA (nm)	DA-DA^{zw}-DA^{zw} (nm)
S_1	263.5	284.2	265.1	286.1	285.5
S_2	224.4	237.2	261.4	261.7	277.9
S_3	211.5	204.5	261.3	260.6	261.7
S_4	200.2	207.5	216.8	236.3	237.0
S_5	197.6	194.0	213.5	230.6	230.6
S_6	193.1	212.9	212.4	229.8	226.7



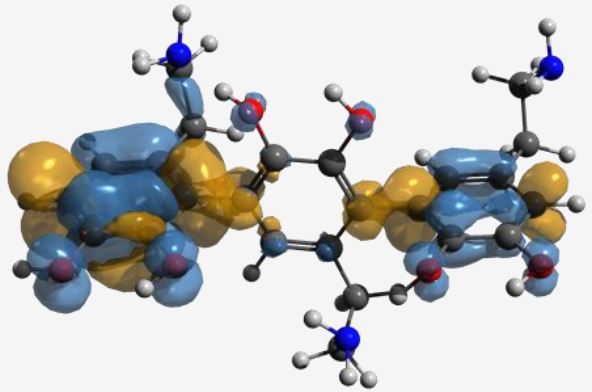
DA-DA-DA:



$S_0 \rightarrow S_1$



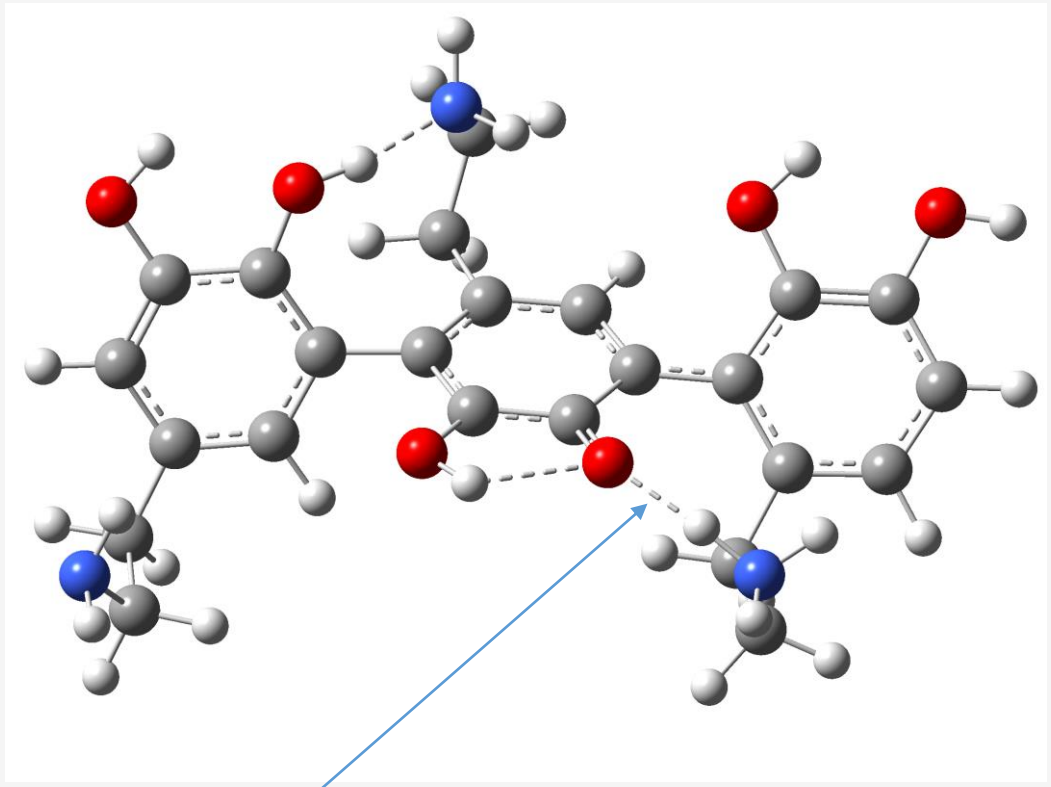
$S_0 \rightarrow S_2$



$S_0 \rightarrow S_3$

Photochemistry of polydopamine polymer (trimer) chains

DA-DA-DA's S_1 optimized geometry:



Internal proton transfer can easily occurs during the excited state relaxation !!!

Fluorescence emission wavelength:

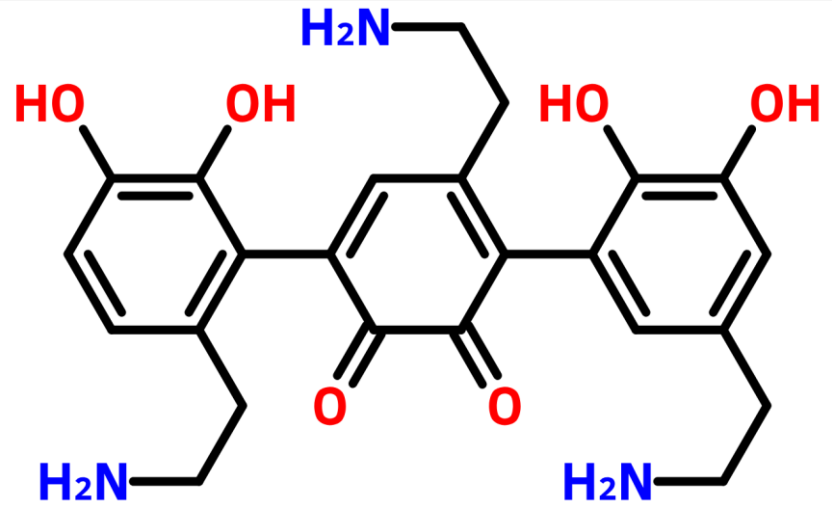
DA:	**λ^{em} = 301.4 nm**
DA-DA-DA:	**λ^{em} = 419.3 (324.4) nm**
DA-DA^{zw}-DA:	**λ^{em} = 419.4 nm**

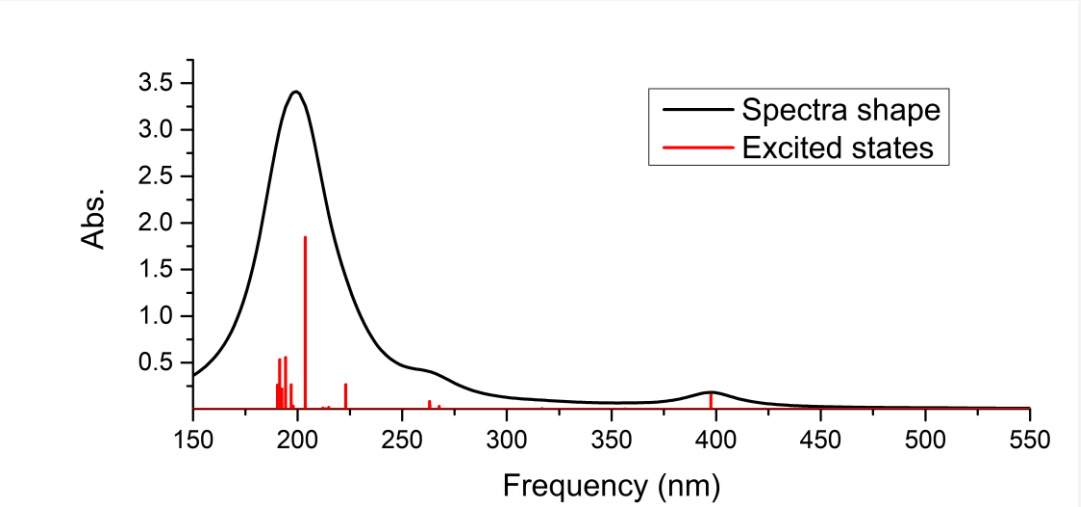
Fluorescence lifetime:

DA:	τ = 3.16 ns
DA-DA-DA:	τ = 7.10 ns
DA-DA^{zw}-DA:	τ = 17.84 ns

Photochemistry of polydopamine polymer (trimer) chains

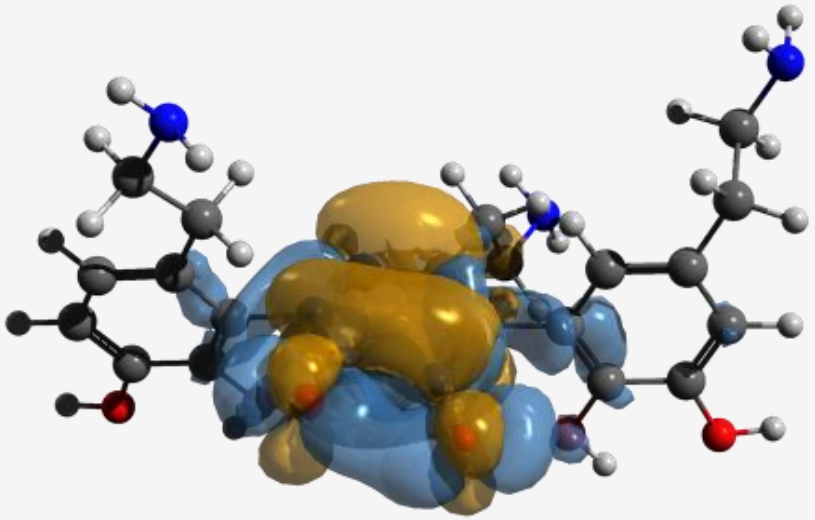
DA-DQ-DA





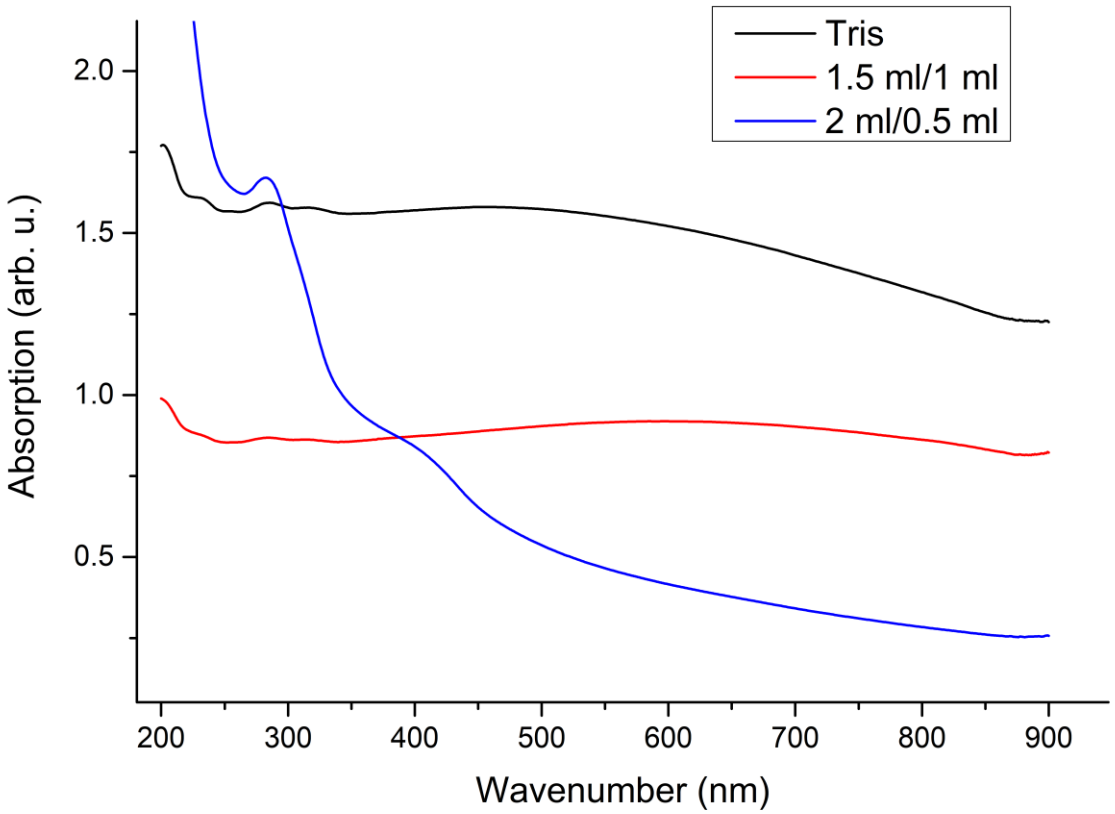
State	ωB97X-D3BJ	SOS-PBE-QIDH
S_1	481.1	506.5
S_2	379.9	397.5
S_3	334.6	439.4
S_4	329.1	423.2
S_5	313.6	356.6
S_6	295.2	331.6
S_7	283.8	330.3
S_8	270.7	316.7
S_9	239.8	263.2
S_{10}	238.9	263.1

λ^{em} = 618 nm



Photochemistry of polydopamine polymer (trimer) chains

Experimental UV-Vis spectra:



Different structural forms can be seen for low and high concentrations

Large band shape due to several slightly different structures (for ex. the position of protonation or deprotonation as well as supramolecular aggregation)

Conclusions:

- Dopamine shows different photochemical behavior depending on its structural configuration (neutral, zwitterionic, protonated, deprotonated);
- Quinone form can drastically influence both the absorption and emission wavelengths and the fluorescence lifetime;
- During polymerization, different forms of dopamine units may exhibit different photochemical behavior, but their average effects mean that the individual fingerprints of each unit cannot be accurately identified

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Thank You for Your Attention