ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxxx

Optical properties of nanostructured antiviral and anti-cancer drugs

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Received Date
Accepted Date

DOI: 00.0000/xxxxxxxxxx

Electronic Supplementary Information

In this part we provide additional information about the systems under investigation.

In Table S1 and Table S2 we report the HOMO-LUMO energies and their gaps as obtained with the DFT calculations. From Table S1 we can see that the energy gap remains almost the same in gas phase and in aqueous solution. The (%) variation of the HOMO-LUMO gap in aqueous solution with respect to the value in gas phase are smaller than 1% for the energy gaps of 5FU, C_{24}, $B_{12}N_{12}$, $C_{23}B$. For T705, $CB_{11}N_{12}$ and $Ga_{12}N_{12}$ the presence of the solvent leads to an increase of the HOMO-LUMO gap (respectively of +1.7%, +1.9% and +4.9%). From this table we can also see that the HOMO-LUMO gap of the C/BN carrier can be modified by heteroatom doping. The aforementioned results show that the B-doping ($C_{24}\rightarrow C_{23}B$) and the C-doping ($B_{12}N_{12}\rightarrow CB_{11}N_{12}$) reduce the energy gap of the nanocarriers, both in gas phase and in aqueous solution. In particular, the substitution of a C atom with a B atom in C_{24} to obtain $C_{23}B$ leads to a reduction of the HOMO-LUMO energy gap (from 2.50 eV to 1.97 eV in gas phase). We find a similar behavior for the systems $B_{12}N_{12}$ and $CB_{11}N_{12}$ (from 6.72 eV to 4.43 eV).

Regarding the combined systems, in Table S2 we see some interesting results. For C_{24}-T705 and the four original systems (C/BN cluster covalently bonded to 5FU) we find similar energy gap value from the two type of calculations (DFT in gas phase and in aqueous solution). In particular, the energy gap of $C_{23}B$-5FU in aqueous solution is smaller than the value in gas phase (-4.9%), while in the other just mentioned four cases the % deviations are smaller than 1%. For the remaining systems (C/BN-T705 and $Ga_{12}N_{12}$-5FU) we see that the energy gap calculated in gas phase and the value obtained in water solution are quite different. In particular, for $B_{12}N_{12}$-T705, the energy gap in aqueous solution is 0.95 eV higher than the value in gas phase. For the systems $C_{23}B$-T705 and $CB_{11}N_{12}$-T705 the energy gaps in gas phase take place, respectively, in IR (1.43 eV) or at the border IR/VIS (1.68 eV) while in aqueous solution these are shifted to the visible (2.24 eV and 2.20 eV, respectively). For the two configurations of $Ga_{12}N_{12}$-5FU, the presence of the solvent leads to an increase of the HOMO-LUMO energy gaps (+0.36 eV and +0.26 eV).

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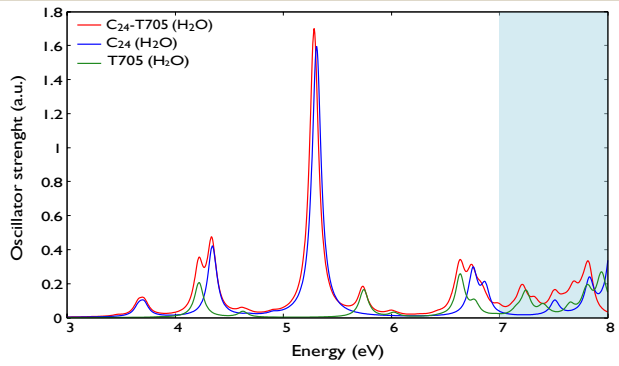
Table S1 Frontier molecular orbital energies, HOMO–LUMO energy gap of free systems. All the values are given in eV

Free systems	Gas phase			Aqueous solution		
	E_{HOMO}	E_{LUMO}	E_{gap}^{HL}	E_{HOMO}	E_{LUMO}	E_{gap}^{HL}
T705	-7.33	-2.70	4.63	-7.33	-2.62	4.71
5FU	-7.28	-1.95	5.32	-7.08	-1.76	5.32
C_{24}	-6.30	-3.81	2.50	-6.17	-3.68	2.49
$B_{12}N_{12}$	-7.95	-1.24	6.72	-7.92	-1.14	6.78
$C_{23}B$	-6.19	-4.21	1.97	-6.05	-4.07	1.98
$CB_{11}N_{12}$	-5.77	-1.33	4.43	-5.74	-1.22	4.52
$Ga_{12}N_{12}$	-6.62	-3.60	3.02	-6.60	-3.44	3.17

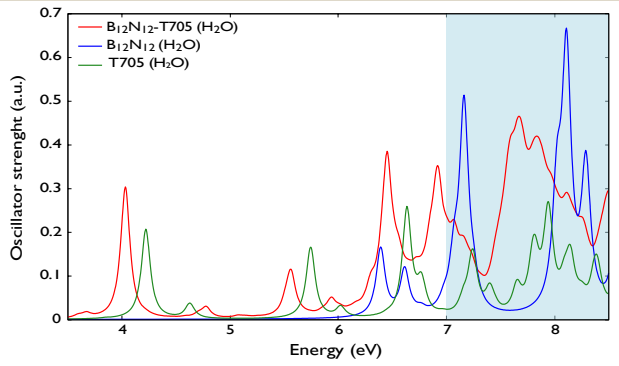
Table S2 Frontier molecular orbital energies, HOMO–LUMO energy gap of the combined systems. All the values are given in eV

Combined systems	Gas phase			Aqueous solution		
	E_{HOMO}	E_{LUMO}	E_{gap}^{HL}	E_{HOMO}	E_{LUMO}	E_{gap}^{HL}
C_{24}-T705	-6.12	-3.62	2.50	-6.16	-3.68	2.48
$B_{12}N_{12}$-T705	-6.89	-3.73	3.16	-7.24	-3.14	4.11
$C_{23}B$-T705	-5.27	-3.84	1.43	-5.59	-3.34	2.24
$CB_{11}N_{12}$-T705	-4.01	-2.33	1.68	-4.24	-2.04	2.20
$Ga_{12}N_{12}$-5FU (ads)	-6.06	-3.17	2.88	-6.34	-3.09	3.25
$Ga_{12}N_{12}$-5FU (cov)	-6.04	-3.02	3.02	-6.31	-3.02	3.29
C_{24}-5FU	-6.58	-4.29	2.29	-6.21	-3.92	2.29
$B_{12}N_{12}$-5FU	-7.48	-2.88	4.60	-7.32	-2.70	4.62
$C_{23}B$-5FU	-6.68	-4.75	1.94	-6.22	-4.37	1.85
$CB_{11}N_{12}$-5FU	-7.16	-2.20	4.96	-7.11	-2.11	5.00

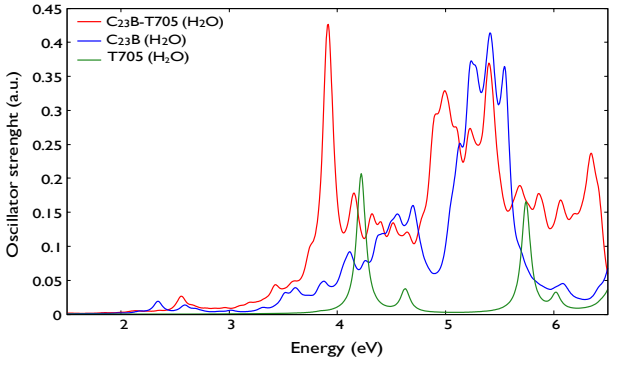
In Figure S1, Figure S2 and Figure S3 we show the absorption spectra of the combined systems together with those of the free molecules, all calculated for the aqueous solution. We have marked the region beyond 7 eV with a blue area to indicate the spectral region in which the water absorbs strongly (absorption coefficient $\sim 10^7 - 10^8\,\mathrm{m}^{-1}$) [1]. If one performs an absorption experiment in water, it will not be possible to recognize peaks in that region because they would probably be obscured by the water absorption. The optical absorption of the solvent is an important point to be considered with respect to possible all-optical applications in drug delivery; *e.g.* in case of transport in blood one should consider the extinction coefficient of the various components, Hemoglobin (Hb), HbO_2, plasma etc.. The modifications arising in the absorption spectra after the drug/carrier occurred bond are not very different in aqueous solution with respect to those for the gas phase. Some peaks may be at different energy and have a different O.S. with respect the gas phase, but the previous discussed general feature are maintained (*e.g.*, the overlap between the spectra of C_{24}-T705 and its carrier; the presence of new absorption structures in the IR region for $B_{12}N_{12}$-5FU; the high energies behavior for $Ga_{12}N_{12}$-5FU).



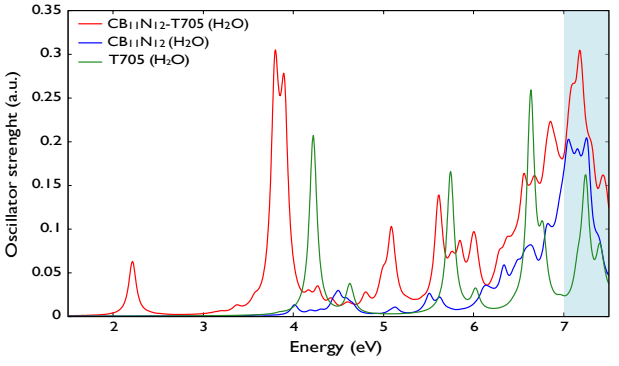
(a) Absorption spectra of C_{24}-T705 (red line) compared to those of the C_{24} (blue line) and T705 (green line) in aqueous solution.



(b) Absorption spectra of $B_{12}N_{12}$-T705 (red line) compared to those of the $B_{12}N_{12}$ (blue line) and T705 (green line) in aqueous solution.

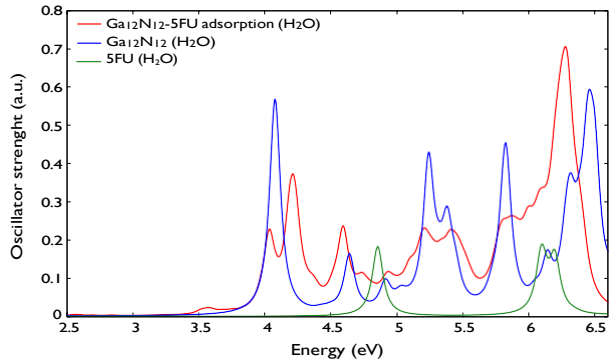


(c) Absorption spectra of $C_{23}B$-T705 (red line) compared to those of the $C_{23}B$ (blue line) and T705 (green line) in aqueous solution.

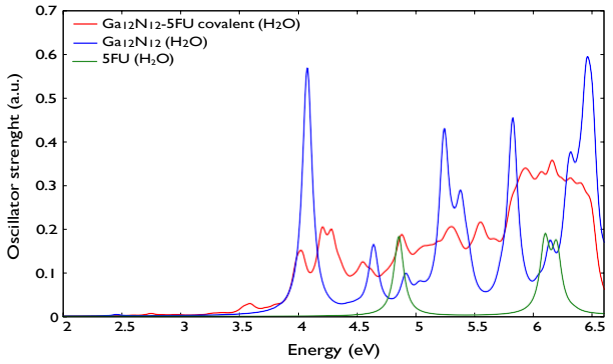


(d) Absorption spectra of $CB_{11}N_{12}$-T705 (red line) compared to those of the $CB_{11}N_{12}$ (blue line) and T705 (green line) in aqueous solution.

Fig. S1 Absorption spectra of the combined systems (a) C_{24}-T705, (b) $B_{12}N_{12}$-T705, (c) $C_{23}B$-T705, (d) $CB_{11}N_{12}$-T705 after Ref[2], together with those of the free molecules (C/BN-carrier and T705). All the spectra are calculated in aqueous solution. The region beyond 7 eV is marked with a blue area to indicate the spectral region in which the water absorbs strongly (see text).

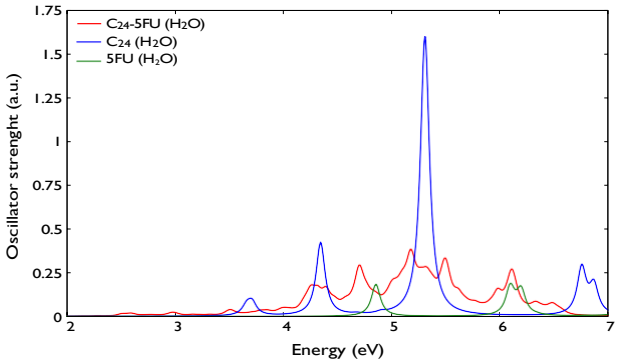


(a) Absorption spectra of the adsorption system $Ga_{12}N_{12}$-5FU (red line), $Ga_{12}N_{12}$ (blue line) and T705 (green line) in aqueous solution.

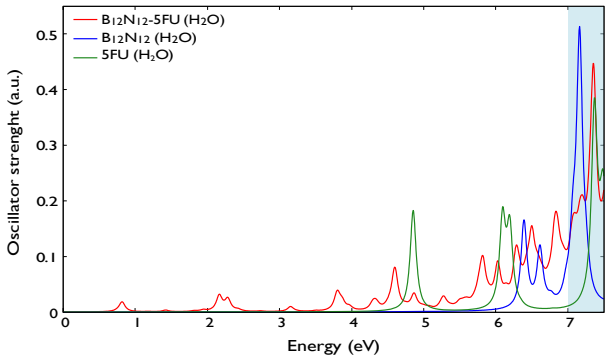


(b) Absorption spectra of the covalent system $Ga_{12}N_{12}$-5FU (red line), $Ga_{12}N_{12}$ (blue line) and T705 (green line) in aqueous solution.

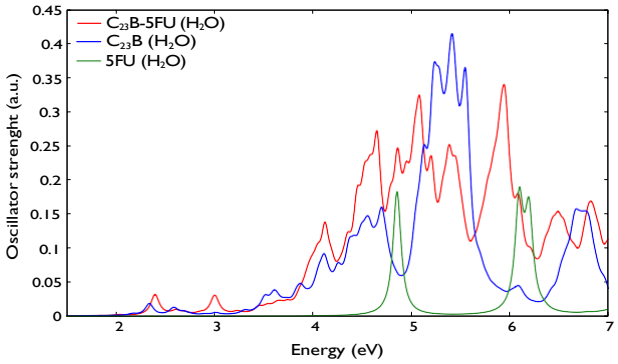
Fig. S2 Absorption spectra of the combined systems $Ga_{12}N_{12}$-5FU (a) with adsorption interaction and (b) with covalent bond after Ref[3], compared to those of the free molecules ($Ga_{12}N_{12}$ carrier and 5FU). All the spectra are calculated in aqueous solution.



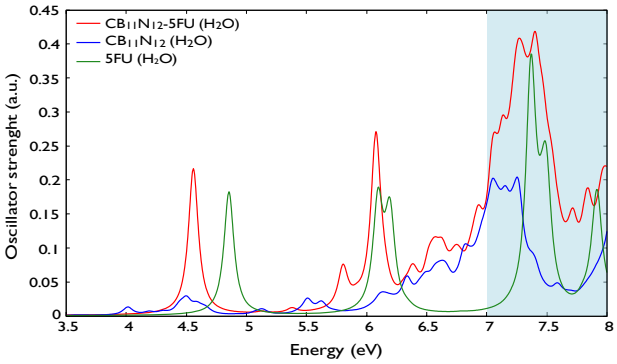
(a) Absorption spectra of C_{24}-5FU (red line) compared to those of the C_{24} (blue line) and 5FU (green line) in aqueous solution.



(b) Absorption spectra of $B_{12}N_{12}$-5FU (red line) compared to those of the $B_{12}N_{12}$ (blue line) and 5FU (green line) in aqueous solution.



(c) Absorption spectra of $C_{23}B$-5FU (red line) compared to those of the $C_{23}B$ (blue line) and 5FU (green line) in aqueous solution.



(d) Absorption spectra of $CB_{11}N_{12}$-5FU (red line) compared to those of the $CB_{11}N_{12}$ (blue line) and 5FU (green line) in aqueous solution.

Fig. S3 Absorption spectra of the combined systems (a) C_{24}-5FU, (b) $B_{12}N_{12}$-5FU, (c) $C_{23}B$-5FU, (d) $CB_{11}N_{12}$-5FU after this work, together with those of the free molecules (C/BN-carrier and 5FU). All the spectra are calculated in aqueous solution. The region beyond 7 eV is marked with a blue area to indicate the spectral region in which the water absorbs strongly (see text).

In the following tables the optimized coordinates for some cases here studied are reported, while the others are available upon request from interested researchers.

Table S3 The optimised molecular specification for C_{24}-T705

Charge = 0		Multiplicity = 1	
C	1.07811207	0.69528113	-1.26871810
C	0.58509503	-0.33070695	-0.30590503
C	0.77350505	0.63008613	0.81791506
C	1.27356208	1.65206620	-0.14310402
C	1.53873911	0.27304810	1.90320914
C	2.86857121	0.91118415	2.12012516
C	2.50001518	2.24627625	0.05521700
C	2.17606615	-1.07801100	1.95588415
C	3.33049024	1.85612122	1.23173409
C	3.50541526	-0.43863296	2.16834016
C	4.46909533	1.53394819	0.32250902
C	3.63638827	1.92049422	-0.85433507
C	4.55707533	-0.73680299	1.33189610
C	5.05506437	0.28995909	0.36997902
C	4.86276736	-0.67183498	-0.75495006
C	3.45814525	1.03568615	-1.89395815
C	1.99717814	-1.96377107	0.91812607
C	2.12808315	0.39690211	-2.10588617
C	1.15940507	-1.58088904	-0.26048402
C	3.13291922	-2.28616710	0.00785500
C	4.09425930	-0.31452095	-1.83922614
C	4.36106532	-1.69535206	0.20635401
C	2.76516120	-0.95373000	-2.05655716
C	2.30321916	-1.89884907	-1.16930110
C	-7.28687454	0.35398112	0.26589702
C	-5.22267441	1.31353019	-0.01076801
C	-4.62741437	0.03323909	-0.12263001
C	-6.68993451	-0.90084898	0.15335101
H	-8.35598764	0.46286813	0.42251903
C	-3.14705425	-0.18646793	-0.33205003
O	-2.35046219	0.74227114	-0.40135304
N	-2.80201723	-1.49529503	-0.43599304
H	-1.82399016	-1.72135305	-0.53418504
H	-3.49889328	-2.21660408	-0.33512303
N	-5.40147644	-1.05884099	-0.03483601
N	-6.53951953	1.45151320	0.18132501
F	-7.44513257	-2.00410506	0.23907801
O	-4.49917035	2.43650027	-0.09286801
H	-5.12945740	3.16891333	0.01227000

Table S4 The optimised molecular specification for C_{23}B-T705

Charge = 0		Multiplicity = 2	
C	0.6041841	0.7499282	1.2596422
C	1.69466928	1.64767232	-1.33924818
C	1.65666828	1.76187133	1.1928172
C	2.54541339	0.9682612	2.10118934
C	3.83739259	0.68406415	1.74624129
C	4.20956163	-0.70579407	1.34743422
C	4.33268165	-0.72584707	-1.16230816
C	2.77483139	-2.26022228	0.02091302
C	3.22400347	-1.68020821	1.31830322
C	1.82509926	-1.40461115	1.71039428
C	1.37672218	-1.96094123	0.36017408
C	3.46825552	0.08359606	-2.05884429
C	2.45405136	-0.9936481	-2.0962773
C	4.38038569	1.19639621	0.45196708
C	4.72782871	-0.18701999	0.06198402
C	3.54594256	1.92671134	-0.37960204
C	3.09370249	1.36495727	-1.68439624
C	2.15294035	2.2570344	-0.01571298
C	1.49219423	-0.09262895	2.05902034
C	3.29973347	-1.78749222	-1.17154616
C	1.14936416	-0.68767902	-1.69669024
C	0.70972611	0.68645818	-1.3934602
C	0.52988006	-1.27213912	-0.48138206
B	-0.12866202	0.19706112	-0.07469
C	-6.59798197	0.60562327	0.01904102
C	-4.41509466	1.30579735	-0.03609498
C	-3.97846062	-0.03908486	-0.01257698
C	-6.14970798	-0.72183694	0.04314702
H	-7.65759416	0.84350731	0.03166002
C	-2.55593539	-0.47149695	-0.02965698
O	-1.65273426	0.41741317	-0.082753
N	-2.32077639	-1.77222415	0.01668302
H	-1.35254023	-2.09034621	-0.06911
H	-3.11087951	-2.40290423	0.03484202
N	-4.88037776	-1.03499701	0.02732102
N	-5.72285684	1.6009294	-0.02022398
F	-7.03859611	-1.71572908	0.08296003
O	-3.55549252	2.32305449	-0.074662
H	-4.08272759	3.13997362	-0.084552

Table S5 The optimised molecular specification for $CB_{11}N_{12}$-T705

Charge = 0		Multiplicity = 2	
B	3.02350219	1.73561517	1.20807707
B	3.43800523	1.72443317	-0.70708407
B	3.63400423	-0.448754	-1.67508315
B	1.96981511	0.42219108	-2.03238818
B	-0.17833506	-0.04114495	-0.51673006
B	1.69874908	-1.74963609	-1.0299641
B	1.29767805	-1.73467308	0.81176704
B	1.13274004	0.44688908	1.81639812
B	3.67081223	-1.7334591	0.36481101
B	2.79397117	-0.42652799	2.19110215
B	4.5132733	-0.01379997	0.53819402
N	2.25007314	2.28291521	0.03463998
N	4.26666529	1.41755914	0.47656801
N	3.33335422	0.99332511	-1.92003317
N	4.46989829	-0.94378204	-0.61567307
N	0.79259302	0.94487912	-1.37998313
N	2.32690013	-1.00545003	-2.10531118
N	0.45230198	-1.42010906	-0.33982405
N	0.33205099	0.95877712	0.73068003
N	2.43204213	-2.39126014	0.09927599
N	1.42403306	-0.97983803	2.04378813
N	2.42353315	1.01731812	2.27569415
N	3.99294926	-0.93186804	1.5795391
C	1.10711105	1.56357217	-0.20573704
C	-6.30408354	0.81146815	0.41505601
C	-4.13444735	1.28591217	-0.15419403
C	-3.82030434	-0.11585594	-0.23570604
C	-5.9965035	-0.54296996	0.343422
H	-7.29549558	1.16556418	0.67089603
C	-2.57131324	-0.67333699	-0.56386507
O	-1.52362916	0.10300607	-0.88738709
N	-2.44182224	-2.02479609	-0.66032207
H	-1.51393117	-2.41787812	-0.60263607
H	-3.2360133	-2.54511013	-0.31039405
N	-4.82140242	-1.029583	0.03653398
N	-5.32893544	1.72712321	0.15868699
F	-6.9695116	-1.43879702	0.60992802
O	-3.17461328	2.20939724	-0.39996405
H	-3.62649031	3.06249231	-0.28758104

Table S6 The optimised molecular specification for C_{24}-5FU

Charge = 0		Multiplicity = 2	
C	4.009027711	-0.010753439	-0.032367126
C	3.530360888	-1.333148878	-0.486738724
C	3.048895162	-0.712945875	-1.760233993
C	3.553530244	0.615110061	-1.291800501
C	1.73703709	-0.854620467	-2.138767835
C	0.809916181	0.313073126	-2.04896478
C	2.682573024	1.69277736	-1.232253361
C	0.786180404	-1.599144273	-1.258446818
C	1.271209138	1.563137215	-1.651711561
C	-0.125318965	-0.464515776	-1.245801892
C	0.847172	2.075213384	-0.298489701
C	2.260021587	2.244411933	0.090908618
C	-0.771219825	0.074880683	0.041378664
C	-0.029996716	1.385870838	0.498779747
C	0.484186635	0.748081652	1.712322209
C	2.724235043	1.667312371	1.265898013
C	1.225282522	-2.209941228	-0.088814943
C	3.644583872	0.505914071	1.210379921
C	2.636775657	-2.03475333	0.308728225
C	0.799875131	-1.618162217	1.230560446
C	1.801008771	0.911376504	2.142684055
C	-0.04993681	-0.545146076	1.296370027
C	2.702903006	-0.259610866	2.065908284
C	2.213422	-1.484696351	1.632122333
C	-2.28217198	0.088856751	0.03147413
C	-3.03458874	-1.036106199	0.031055115
C	-4.292041116	1.499982369	-0.022833449
C	-4.494246797	-1.006062798	0.002966329
N	-2.913043808	1.318630319	-0.001021619
N	-5.000411401	0.306559253	-0.02612878
O	-5.230028759	-1.978096263	0.001826777
O	-4.814275993	2.60162207	-0.036728348
F	-2.445871674	-2.247080278	0.049681606
H	-6.012091271	0.394065251	-0.043892054
H	-2.358489881	2.166780514	0.040154372

Table S7 The optimised molecular specification for $C_{23}B$-5FU

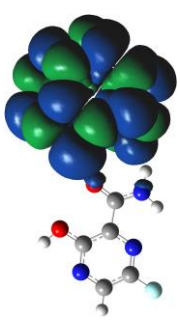
Charge = 0		Multiplicity = 1	
C	4.104082782	-0.068528347	-0.002398135
C	3.588865635	-1.020322918	1.00295623
C	3.112883473	-1.936951026	-0.079806503
C	3.589809275	-0.934394131	-1.083066238
C	1.792719985	-2.286573552	-0.095002401
C	0.838403388	-1.737286232	-1.118444261
C	2.733766738	-0.413782284	-2.035390511
C	0.837488351	-1.823328927	0.968689129
C	1.312547695	-0.783014107	-2.0122737
C	-0.040478244	-1.274224848	-0.054553939
C	0.902921554	0.683872949	-1.9928333
C	2.325042925	1.024258639	-1.940297443
B	-0.8404521	0.149105824	0.002358341
C	0.030009545	1.133628842	-1.022552057
C	0.585124462	1.943528704	0.07776586
C	2.836853775	1.872904673	-0.972916246
C	1.309871177	-0.946323531	1.938767541
C	3.713312214	1.269253416	0.052439815
C	2.731162432	-0.579628122	1.993484426
C	0.899956956	0.517741836	2.038207424
C	1.923567949	2.347552262	0.095335628
C	0.02858179	1.045711357	1.106724465
C	2.83552224	1.786773445	1.12241426
C	2.321899311	0.860990212	2.015455915
C	-2.433657517	0.115830642	-0.001705971
C	-3.177509529	-1.016516409	0.001417717
C	-4.494677165	1.475481392	-0.005212122
C	-4.636486706	-1.031532171	0.004234428
N	-3.116532725	1.325516041	-0.00433976
N	-5.176963102	0.266114334	0.001160888
O	-5.351152617	-2.021975618	0.00895345
O	-5.049810323	2.564178413	-0.011057881
F	-2.575226895	-2.233306547	0.003400667
H	-6.190196753	0.329540498	0.001514901
H	-2.597833312	2.194923719	-0.013465105

Table S8 The optimised molecular specification for $CB_{11}N_{12}$-5FU

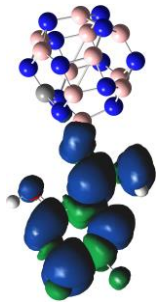
Charge = 0		Multiplicity = 1	
B	0.877201241	-0.369396834	1.945261535
B	2.612654245	0.441040309	1.977010079
B	3.938384431	0.021440624	-9.71196E-05
B	0.894449488	1.761498535	0.959297493
B	3.091889306	1.75023071	0.000912647
B	0.894289723	1.762654688	-0.957180216
B	2.612499355	0.443352446	-1.976616236
B	0.877119012	-0.367142052	-1.945634354
C	-0.730983391	0.031085285	4.46848E-06
B	2.60804063	-1.752115706	-0.959916945
B	0.422798632	-1.67888406	-0.000905799
B	2.608086738	-1.753215344	0.957727323
N	1.255870774	1.042304658	2.138841911
N	2.222390686	-0.984186611	2.112559327
N	3.652613836	0.952600658	1.123561251
N	3.685453977	-1.395346837	-0.000905971
N	1.812423531	2.418344864	0.001373667
N	3.652557741	0.95393047	-1.122655071
N	1.255715356	1.044768455	-2.137537305
N	-0.173306386	1.382456937	0.000887658
N	2.222260705	-0.981742929	-2.113850436
N	-0.149000583	-0.866504211	-1.083303168
N	-0.149038369	-0.867824504	1.082528892
N	1.668492871	-2.389740291	-0.0014187
C	-2.255721317	0.049469941	3.42625E-05
C	-3.03831537	-1.055276846	-1.56007E-05
C	-4.222596392	1.520407687	-3.04061E-05
C	-4.499569353	-0.975520555	-7.52961E-05
N	-2.854063001	1.294515921	0.000333787
N	-4.968194732	0.34853855	-0.000989873
O	-5.261032933	-1.927948839	0.000466278
O	-4.713778673	2.63700905	0.000203202
F	-2.513053969	-2.292382203	-4.54406E-05
H	-5.977010829	0.465603979	-0.000622844
H	-2.250194516	2.110238602	0.000897576

1 Spin density plots

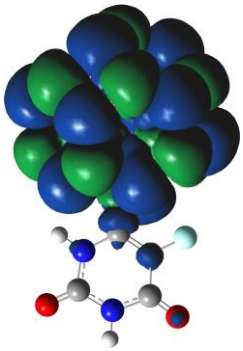
In the following figures the spin density plots have been reported for the open-shell systems $C_{23}B$-T705, $CB_{11}N_{12}$-T705,C_{24}-5FU, $B_{12}N_{12}$-5FU. The different colors represents the different spin direction.



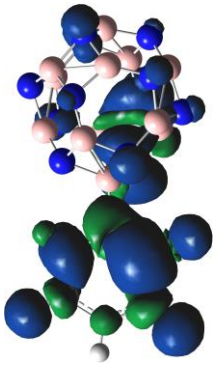
(a) Spin density plot of $C_{23}B$-T705



(b) Spin density plot of $CB_{11}N_{12}$-T705



(c) Spin density plot of C_{24}-5FU



(d) Spin density plot of $B_{12}N_{12}$-5FU

Fig. S4 Spin density plots of the open-shell systems (a) $C_{23}B$-T705, (b) $CB_{11}N_{12}$-T705, (c) C_{24}-5FU, (d) $B_{12}N_{12}$-5FU

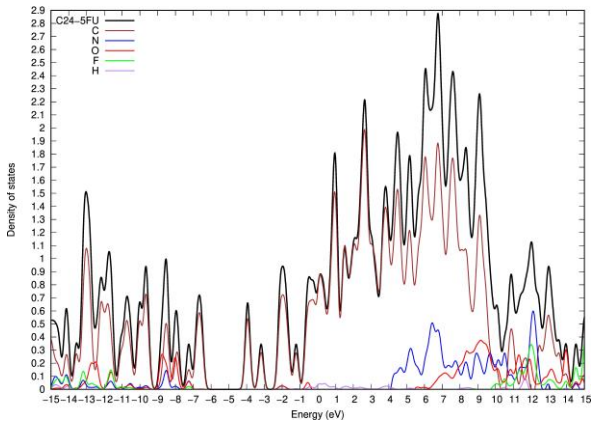
2 Density of States

In this section we report the Projected Density of States of the main compounds carriers of 5FU (C_{24}-5FU, $B_{12}n_{12}$-5FU, $B_{11}N_{12}C$-5FU) and the PDOS for the C_{24}-T705 as comparison with the same carrier and different drug.

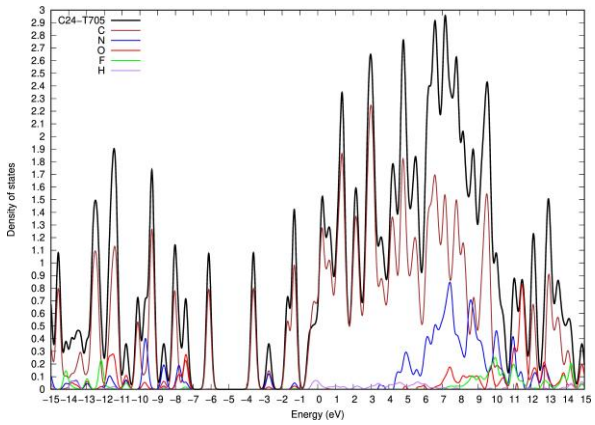
For both C_{24}-5FU and C_{24}-T705 in the gap region there is a fundamental contribution given by C atoms, while for the Nitrogen contributions the dominant part relies in the region 4 to 12 eV. In the same region appears also an important contribution by O atoms. For both atoms there are also absorption structures due to O and N in the region of few eV below the gap. For the Fluorine atom a not negligible contribution appears just in the 10-15 eV for the C_{24}-5FU and in the 7-15 eV for the C_{24}-T705.

In the case of the $B_{12}n_{12}$-5FU, and $B_{11}N_{12}C$-5FU the main contribution to the DOS is due to B and N atoms with a significative contribution of the C atoms (at leas in the region upper the gap) while O and F contribution are present just in the 6-15 eV region.

Even in the case of these two last compounds the states at the edge of the gap are mainly due to the C and O atoms.

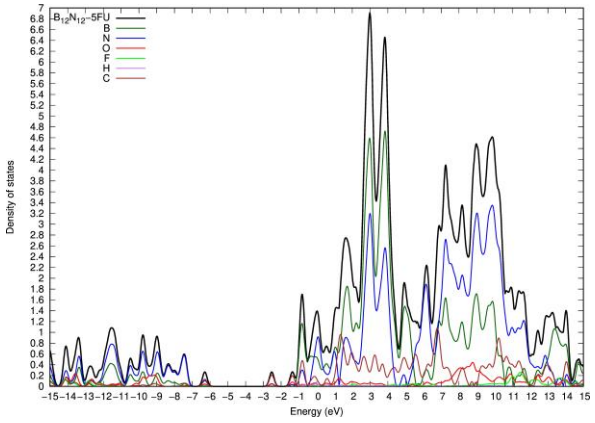


(a) PDOS C_{24}-5FU

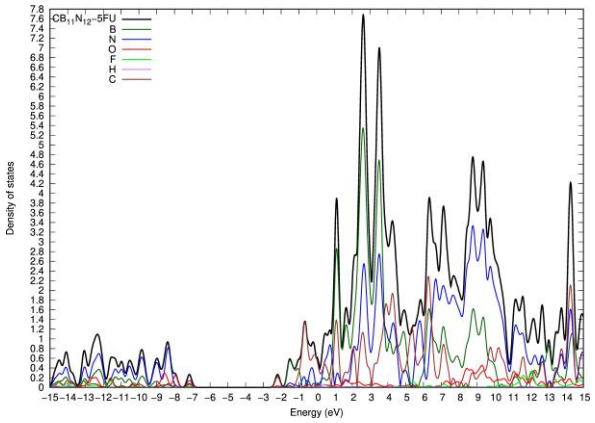


(b) PDOS C_{24}-T705

Fig. S5 Projected Density of Representation of (a) C_{24}-5FU and (b) C_{24}-T705. All the PDOS are reported in arbitrary units



(a) PDOS $B_{12}N_{12}$-5FU



(b) PDOS $CB_{11}N_{12}$-T705

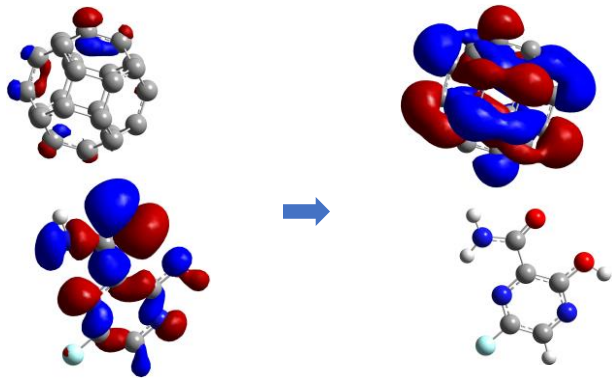
Fig. S6 Projected Density of Representation of (a) $B_{12}n_{12}$-5FU and (b) $B_{11}N_{12}C$-5FU. All the PDOS are reported in arbitrary units

3 Orbitals

In this part of our work we report the Molecular Orbitals (MO) related to the optical onset transitions for some of the compounds under study.

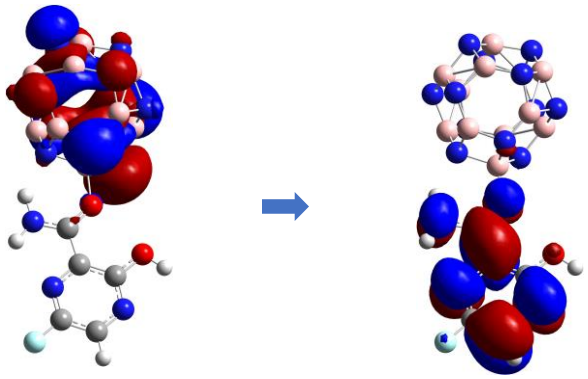
For some compounds (C_{24}-T705, $B_{12}N_{12}$-T705, $C_{23}B$-T705, $B_{12}n_{12}$-5FU and the adsorbed configuration of the $Ga_{12}N_{12}$-5FU) we found a clear charge transfer after the optical transition, but we did not find the same behavior for the other molecules under investigations ($B_{11}N_{12}C$-T705, C_{24}-5FU, $C_{23}B$-5FU, $B_{11}N_{12}C$-5FU and the covalent linked $Ga_{12}N_{12}$-5FU).

There is no clear indication that charge transfer occurs with specific drug linked to the carrier (there are charge transfer transition for both 5FU and T705) but in some case (*e.g.* $Ga_{12}N_{12}$-5FU) we found that with the same carrier and drug the charge transfer occurs in the case of adsorbed configuration but not in the case of covalent bond between carrier and drug.



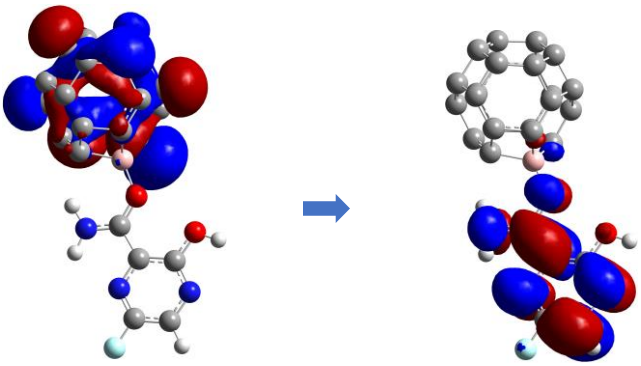
(a) HOMO-3 of C_{24}-T705 **(b)** LUMO+1 of C_{24}-T705

Fig. S7 Representation of (a) starting and (b) final state for onset transition of C_{24}-T705.



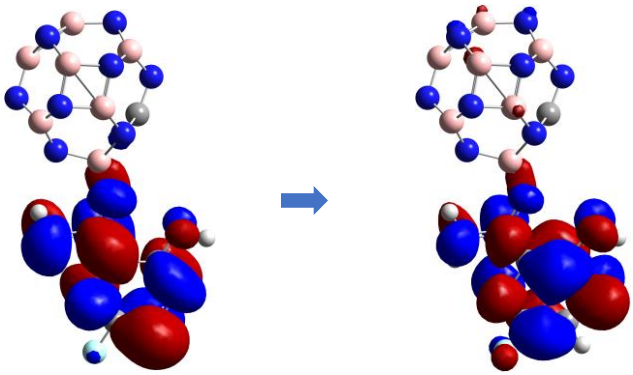
(a) HOMO of $B_{12}N_{12}$-T705 **(b)** LUMO of $B_{12}N_{12}$-T705

Fig. S8 Representation of (a) starting and (b) final state for onset transition of $B_{12}N_{12}$-T705.



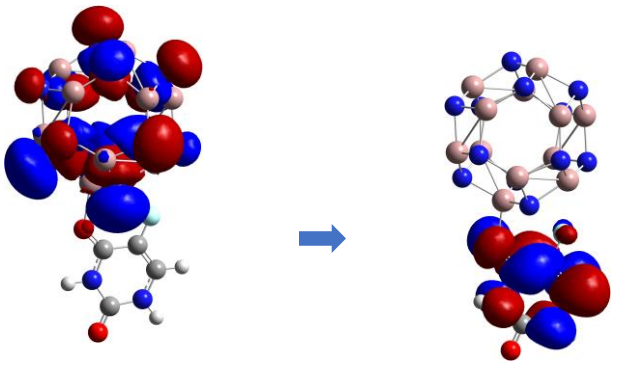
(a) HOMO of $C_{23}B$-T705 **(b)** LUMO of $C_{23}B$-T705

Fig. S9 Representation of (a) starting and (b) final state for onset transition of $C_{23}B$-T705.



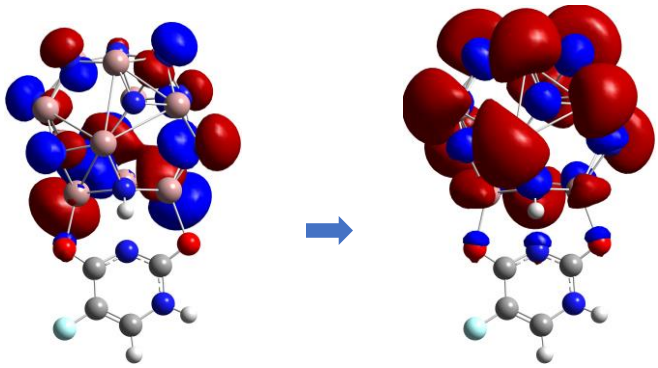
(a) HOMO of $CB_{11}N_{12}$-T705 **(b)** LUMO+9 of $CB_{11}N_{12}$-T705

Fig. S10 Representation of (a) starting and (b) final state for onset transition of $CB_{11}N_{12}$-T705.



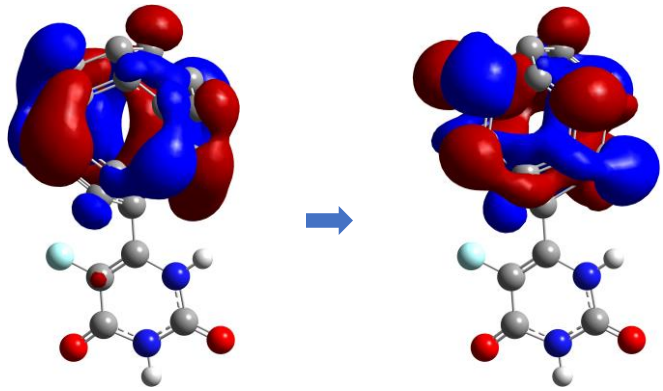
(a) HOMO/HOMO-1 of $Ga_{12}N_{12}$-5FU (adsorption) **(b)** LUMO of $Ga_{12}N_{12}$-5FU (adsorption)

Fig. S11 Representation of (a) starting and (b) final state for onset transition of $Ga_{12}N_{12}$-5FU (adsorption).



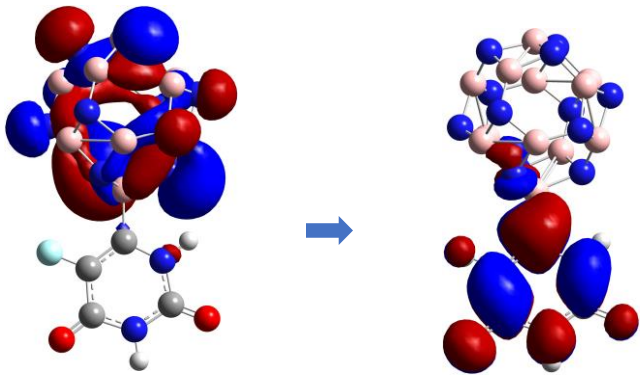
(a) HOMO of $Ga_{12}N_{12}$-5FU (covalent) **(b)** LUMO of $Ga_{12}N_{12}$-5FU (covalent)

Fig. S12 Representation of (a) starting and (b) final state for onset transition of $Ga_{12}N_{12}$-5FU (covalent).



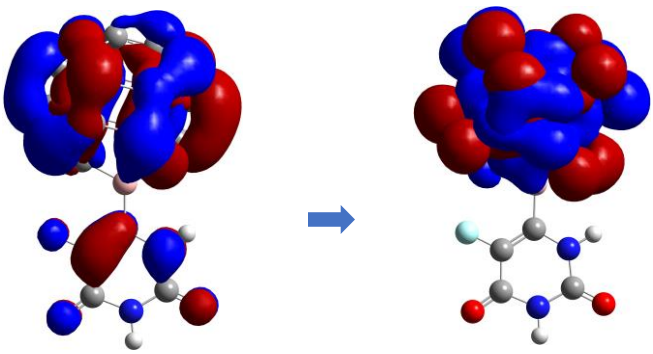
(a) HOMO-2 of C_{24}-5FU **(b)** LUMO of C_{24}-5FU

Fig. S13 Representation of (a) starting and (b) final state for onset transition of C_{24}-5FU.



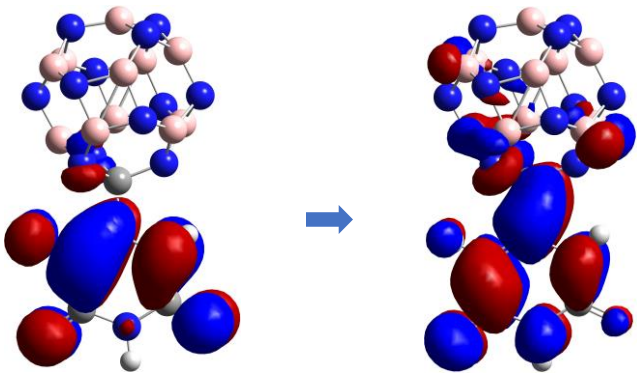
(a) HOMO of $B_{12}N_{12}$-5FU **(b)** LUMO of $B_{12}N_{12}$-5FU

Fig. S14 Representation of (a) starting and (b) final state for onset transition of $B_{12}N_{12}$-5FU.



(a) HOMO/HOMO-2 of $C_{23}B$-5FU **(b)** LUMO+1/LUMO+2 of $C_{23}B$-5FU

Fig. S15 Representation of (a) starting and (b) final state for onset transition of $C_{23}B$-5FU.



(a) HOMO of $CB_{11}N_{12}$-5FU **(b)** LUMO of $CB_{11}N_{12}$-5FU

Fig. S16 Representation of (a) starting and (b) final state for onset transition of $CB_{11}N_{12}$-5FU.

Notes and references

1 K. Be´c and C. Huck, *Frontiers in Chemistry*, 2019, **7**, 48.

2 K. A. Soliman and S. A. Aal, *Diamond and Related Materials*, 2021, **117**, 108458.

3 N. Wazzan, K. Soliman and W. Abdel Halim, *Journal of Molecular Modeling*, 2019, **25**, 265.