SUPPORTING INFORMATION

Theoretical investigations on one- and two-photon absorptions for a series of covalently functionalized hybrid materials based on graphene

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On the basis of the optimized molecular geometries, we calculate the OPA spectra (UV-Vis spectra) of all the molecules in this study by means of the TD-DFT//CAM-B3LYP/6-31G* approach and ZINDO method for comparison. The maximum OPA wavelengths (λ^{O}_{max}), oscillator strengths (*f*), transition nature, and available experimental data for each molecule are all collected in Table S1.

It can be seen from Table S1 that the results of TPP and G1 obtained by the ZINDO method which are in better agreement with experimental data, have the similar changing trends, in comparison with these acquired by the TD-DFT method. The same case also appears in the Gn molecules as well as the hybrid molecules. For example, for the G4 molecule, the

OPA peaks obtained by the ZINDO method are at 328.2 and 267.2 nm, respectively, corresponding to the spectral peaks calculated by the TD-DFT method at 327.4 and 281.0 nm. Furthermore, the changing trends of the OPA spectra of the hybrid molecules by ZINDO are also in accordance with these by TD-DFT. The spectra of the hybrids have multiple peaks because of their special structures, which not only remain the features of each fragment (porphyrin and Gn) but also display new characteristics resulting from the interaction between the two moieties. Thus, all the hybrids mainly have three absorption peaks by TD-DFT. The first one is in the long wavelength range with a bathochromic-shift from TPP-NHCO-G1 to TPP-NHCO-G5, that is at ～ 524.0 – 1067.0 nm, then the second one is around 350 – 370 nm, and the third one is about at 300 – 330 nm. Moreover, the spectral peculiarity can be also observed from the results by ZINDO, which the first peak occurs at ～ 388.7 – 637.8 nm with a bathochromic-shift from TPP-NHCO-G1 to TPP-NHCO-G5, the second one is around 310 nm, and third one is nearby at ～ 300 nm. For example, for the TPP-NHCO-G1 molecule, there are multiple absorption peaks from the results of both methods. The first peak at 388.7 nm by ZINDO, corresponding to that at 365.6 nm by TD-DFT, reflects the properties of porphyrin, and the second peak at ～ 320.2 – 326.1 nm corresponding to ～ 300 nm by TD-DFT is caused by the intramolecular charge transfer between the porphyrin part and the G1

fragment, which is detailedly discussed afterwards, and then the third peak at 273.4 – 279.9 nm is in parallel with that by TD-DFT at 271.2 nm.

Therefore, it can be concluded that the results obtained by the ZINDO method can commendably reflect the UV-Vis electronic spectra. Thus, in this work, we perform the calculations on the OPA and TPA properties of all studied molecules by the ZINDO method.

Table S1 Calculated one-photon absorption spectra by both TD-DFT and ZINDO methods

Molecule	**TD-DFT**		**ZINDO**				
	λ^{O}_{max}/nm	*f*	λ^{O}_{max}/nm	*f*	channel	Transition nature	
TPP	583.8	0.01	584.2	0.002	$S_0 \rightarrow S_2$	(HOMO-1)→(LUMO+1)	42.6%
						(HOMO)→(LUMO)	51.2%
	363.8	1.28	382.7	1.46	$S_0 \rightarrow S_7$	(HOMO-1)→(LUMO)	38.1%
						(HOMO)→(LUMO+1)	38.6%
	354.4	1.66	380.6	1.62	$S_0 \rightarrow S_8$	(HOMO-1)→(LUMO+1)	45.5%
			(419[39,40])			(HOMO)→(LUMO)	37.2%
TPP-NH_2	595.6	0.01	581.2	0.001	$S_0 \rightarrow S_2$	(HOMO-1)→(LUMO+1)	42.8%
						(HOMO)→(LUMO)	50.9%
	540.0	0.03	396.3	0.003	$S_0 \rightarrow S_5$	(HOMO-6)→(LUMO)	12.1%
						(HOMO)→(LUMO+9)	17.7%
						(HOMO,HOMO)→(LUMO,LUMO+1)	31.6%
	369.7	1.31	382.3	1.53	$S_0 \rightarrow S_7$	(HOMO-1)→(LUMO)	31.4%
						(HOMO)→(LUMO+1)	31.9%
	360.2	1.65	379.6	1.49	$S_0 \rightarrow S_8$	(HOMO-1)→(LUMO+1)	35.2%
						(HOMO)→(LUMO)	29.0%
G1			406.1	0.11	$S_0 \rightarrow S_1$	(HOMO)→(LUMO)	86.2%
	264.1	3.59	279.7	2.66	$S_0 \rightarrow S_9$	(HOMO-2)→(LUMO)	51.3%
			(273[38])			(HOMO)→(LUMO+2)	38.7%
G2			506.2	0.36	$S_0 \rightarrow S_2$	(HOMO)→(LUMO)	85.5%
	307.7	1.49	323.4	1.22	$S_0 \rightarrow S_{11}$	(HOMO-4)→(LUMO)	20.2%
						(HOMO-2)→(LUMO)	33.7%
						(HOMO)→(LUMO+2)	20.9%
			270.0	0.52	$S_0 \rightarrow S_{25}$	(HOMO-6)→(LUMO)	28.2%
						(HOMO-1)→(LUMO+4)	10.3%
			245.7	0.67	$S_0 \rightarrow S_{34}$	(HOMO-2)→(LUMO+2)	38.2%
G3			625.2	0.25	$S_0 \rightarrow S_2$	(HOMO)→(LUMO)	86.1%
			350.1	0.69	$S_0 \rightarrow S_{15}$	(HOMO-2)→(LUMO)	31.3%

						(HOMO)→(LUMO+2)	22.2%
	330.3	1.78	324.6	0.90	$S_0 \rightarrow S_{19}$	(HOMO)→(LUMO+6)	35.2%
						(HOMO-1,HOMO)→(LUMO,LUMO)	22.1%
			313.7	0.32	$S_0 \rightarrow S_{21}$	(HOMO-1)→(LUMO+3)	22.6%
						(HOMO,HOMO)→(LUMO,LUMO+1)	12.5%
	289.6	0.56	308.9	0.35	$S_0 \rightarrow S_{23}$	(HOMO-3)→(LUMO)	30.8%
						(HOMO)→(LUMO+6)	12.8%
	245.6	0.83	295.5	0.19	$S_0 \rightarrow S_{29}$	(HOMO-7)→(LUMO)	32.3%
			286.2	0.19	$S_0 \rightarrow S_{32}$	(HOMO-3,HOMO)→(LUMO,LUMO)	22.2%
			255.4	0.22	$S_0 \rightarrow S_{47}$	(HOMO-3)→(LUMO+2)	13.0%
						(HOMO-2)→(LUMO+2)	27.5%
G4			709.7	0.39	$S_0 \rightarrow S_2$	(HOMO)→(LUMO)	84.8%
			380.9	0.67	$S_0 \rightarrow S_{14}$	(HOMO-3)→(LUMO)	10.4%
						(HOMO)→(LUMO+6)	34.3%
			362.2	0.49	$S_0 \rightarrow S_{17}$	(HOMO-6)→(LUMO)	20.7%
						(HOMO)→(LUMO+9)	10.9%
	327.4	1.40	328.2	1.42	$S_0 \rightarrow S_{27}$	(HOMO-7)→(LUMO)	20.4%
						(HOMO)→(LUMO+7)	13.5%
	281.0	0.83	267.2	0.55	$S_0 \rightarrow S_{57}$	(HOMO-9)→(LUMO)	10.0%
						(HOMO-2)→(LUMO+1)	11.9%
G5			788.1	0.38	$S_0 \rightarrow S_2$	(HOMO)→(LUMO)	84.2%
			416.8	1.07	$S_0 \rightarrow S_{14}$	(HOMO)→(LUMO+5)	24.3%
			374.0	0.32	$S_0 \rightarrow S_{19}$	(HOMO-7)→(LUMO)	13.4%
						(HOMO-2)→(LUMO+2)	10.3%
						(HOMO)→(LUMO+7)	16.5%
						(HOMO-2,HOMO)→(LUMO,LUMO)	20.6%
	354.2	0.87	359.2	0.58	$S_0 \rightarrow S_{23}$	(HOMO-1)→(LUMO+2)	22.1%
						(HOMO)→(LUMO+5)	18.1%
			358.2	0.54	$S_0 \rightarrow S_{24}$	(HOMO-1)→(LUMO+1)	52.6%
						(HOMO)→(LUMO+10)	12.6%
	303.6	2.07	326.9	0.45	$S_0 \rightarrow S_{35}$	(HOMO-8)→(LUMO)	45.1%
						(HOMO)→(LUMO+8)	18.8%
			266.3	0.22	$S_0 \rightarrow S_{77}$	(HOMO-3,HOMO)→(LUMO,LUMO+1)	15.6%
						(HOMO-1,HOMO-1)→(LUMO,LUMO+1)	23.4%
			256.5	0.26	$S_0 \rightarrow S_{89}$	(HOMO-6)→(LUMO+2)	13.8%
			250.8	0.69	$S_0 \rightarrow S_{97}$	(HOMO-6)→(LUMO+2)	10.7%
TPP-NHCO-G1	524.0	0.07	388.7	0.12	$S_0 \rightarrow S_9$	(HOMO-2)→(LUMO+1)	60.8%
						(HOMO-2)→(LUMO+2)	25.2%
	365.6	1.72					
	356.6	1.85	326.1	1.52	$S_0 \rightarrow S_{20}$	(HOMO-10)→(LUMO)	12.1%
						(HOMO-1)→(LUMO)	30.1%
						(HOMO)→(LUMO+1)	10.9%
						(HOMO)→(LUMO+2)	24.8%

	300.5	0.81	320.2	1.94	$S_0 \rightarrow S_{23}$	(HOMO-1)→(LUMO)	14.8%
						(HOMO-1)→(LUMO+2)	32.2%
						(HOMO)→(LUMO)	37.5%
			293.6	0.79	$S_0 \rightarrow S_{29}$	(HOMO-10)→(LUMO)	21.6%
						(HOMO-8)→(LUMO)	14.4%
						(HOMO-3)→(LUMO)	10.0%
	281.6	0.53	279.9	0.99	$S_0 \rightarrow S_{35}$	(HOMO-2)→(LUMO+4)	14.5%
						(HOMO)→(LUMO+1)	12.0%
	271.2	1.29	273.4	0.83	$S_0 \rightarrow S_{37}$	(HOMO-2)→(LUMO+6)	32.5%
TPP-NHCO-G2	615.3	0.36	449.7	0.12	$S_0 \rightarrow S_5$	(HOMO)→(LUMO)	26.2%
						(HOMO,HOMO)→(LUMO,LUMO)	37.6%
	532.0	0.03	439.7	0.28	$S_0 \rightarrow S_7$	(HOMO)→(LUMO)	61.9%
						(HOMO,HOMO)→(LUMO,LUMO)	15.5%
	365.6	1.68	317.6	1.71	$S_0 \rightarrow S_{27}$	(HOMO-12)→(LUMO+1)	13.3%
						(HOMO-2)→(LUMO+1)	29.7%
						(HOMO)→(LUMO+3)	35.7%
	356.8	1.73	311.7	2.10	$S_0 \rightarrow S_{28}$	(HOMO-2)→(LUMO+2)	45.5%
						(HOMO-1)→(LUMO+2)	36.8%
	310.3	1.03	297.6	1.14	$S_0 \rightarrow S_{33}$	(HOMO-4)→(LUMO)	31.7%
						(HOMO)→(LUMO+4)	23.2%
			284.3	0.46	$S_0 \rightarrow S_{43}$	(HOMO-12)→(LUMO+1)	16.7%
						(HOMO-10)→(LUMO+1)	11.8%
	273.4	0.63	257.5	0.55	$S_0 \rightarrow S_{65}$	(HOMO-3)→(LUMO+5)	12.0%
						(HOMO-3)→(LUMO+7)	11.6%
						(HOMO,HOMO)→(LUMO,LUMO+3)	11.0%
TPP-NHCO-G3	863.9	0.25	547.8	0.04	$S_0 \rightarrow S_2$	(HOMO)→(LUMO)	10.7%
						(HOMO,HOMO)→(LUMO,LUMO)	47.8%
	531.6	0.03	526.4	0.33	$S_0 \rightarrow S_4$	(HOMO-2,HOMO)→(LUMO,LUMO+2)	12.5%
						(HOMO-1,HOMO)→(LUMO,LUMO+1)	58.4%
						(HOMO-1,HOMO)→(LUMO,LUMO+1)	19.5%
	382.3	0.13	320.6	1.29	$S_0 \rightarrow S_{31}$	(HOMO-8)→(LUMO)	19.5%
						(HOMO-2)→(LUMO+1)	11.1%
						(HOMO-1)→(LUMO+2)	13.3%
						(HOMO)→(LUMO+8)	10.7%
	365.5	1.80	319.2	1.12	$S_0 \rightarrow S_{32}$	(HOMO-8)→(LUMO)	15.6%
						(HOMO-2)→(LUMO+1)	10.5%
						(HOMO-1)→(LUMO+2)	12.6%
						(HOMO)→(LUMO+8)	11.3%
	356.4	1.92	315.8	1.11	$S_0 \rightarrow S_{34}$	(HOMO-4)→(LUMO)	12.9%
						(HOMO-2)→(LUMO+2)	10.1%
	331.1	1.66	310.6	1.13	$S_0 \rightarrow S_{35}$	(HOMO-3)→(LUMO+8)	10.1%
						(HOMO)→(LUMO+20)	18.8%

						(HOMO,HOMO)→(LUMO,LUMO+4)	10.3%
	299.9	0.40	285.8	1.25	$S_0 \rightarrow S_{54}$	(HOMO-13)→(LUMO+1)	18.3%
						(HOMO-11)→(LUMO+1)	12.7%
TPP-NHCO-G4	1067.0	0.39	681.3	0.01	$S_0 \rightarrow S_1$	(HOMO-4)→(LUMO)	12.3%
						(HOMO)→(LUMO+4)	13.0%
						(HOMO,HOMO)→(LUMO,LUMO)	50.8%
	438.3	0.11	583.9	0.60	$S_0 \rightarrow S_3$	(HOMO)→(LUMO)	85.1%
	376.8	0.12	375.3	0.17	$S_0 \rightarrow S_{20}$	(HOMO-3)→(LUMO+3)	16.3%
						(HOMO)→(LUMO+5)	12.1%
						(HOMO)→(LUMO+6)	48.2%
			350.1	0.26	$S_0 \rightarrow S_{28}$	(HOMO)→(LUMO+8)	34.9%
			333.2	0.68	$S_0 \rightarrow S_{32}$	(HOMO-9)→(LUMO)	28.7%
	366.2	1.52	316.2	1.16	$S_0 \rightarrow S_{45}$	(HOMO-2)→(LUMO+1)	19.1%
						(HOMO-1)→(LUMO+2)	23.0%
	356.1	1.85	310.9	2.07	$S_0 \rightarrow S_{48}$	(HOMO-2)→(LUMO+2)	29.7%
						(HOMO-1)→(LUMO+2)	23.8%
	330.3	1.27	295.4	1.62	$S_0 \rightarrow S_{58}$	(HOMO-6)→(LUMO)	10.5%
						(HOMO-3)→(LUMO+3)	41.7%
	301.2	0.51	282.1	0.73	$S_0 \rightarrow S_{70}$	(HOMO-16)→(LUMO+1)	25.8%
						(HOMO-12)→(LUMO+1)	18.0%
						(HOMO-2)→(LUMO+1)	13.0%
TPP-NHCO-G5	1356.7	0.44	785.0	0.02	$S_0 \rightarrow S_1$	(HOMO-4)→(LUMO)	12.6%
						(HOMO)→(LUMO+4)	12.7%
						(HOMO,HOMO)→(LUMO,LUMO)	48.9%
	522.7	0.08	637.8	0.68	$S_0 \rightarrow S_3$	(HOMO)→(LUMO)	83.8%
	471.1	0.22	389.8	0.24	$S_0 \rightarrow S_{19}$	(HOMO-5)→(LUMO)	11.1%
						(HOMO-3)→(LUMO+3)	15.6%
						(HOMO)→(LUMO+5)	52.4%
			376.7	0.66	$S_0 \rightarrow S_{24}$	(HOMO)→(LUMO+7)	32.1%
						(HOMO-3,HOMO)→(LUMO,LUMO)	14.0%
	365.4	1.77	361.8	0.42	$S_0 \rightarrow S_{27}$	(HOMO-12)→(LUMO)	11.3%
						(HOMO-7)→(LUMO)	14.7%
						(HOMO)→(LUMO+11)	23.8%
	357.1	1.66	313.9	2.12	$S_0 \rightarrow S_{55}$	(HOMO-2)→(LUMO+1)	12.1%
						(HOMO-1)→(LUMO+2)	14.2%
	307.0	0.85	305.9	1.15	$S_0 \rightarrow S_{62}$	(HOMO-15)→(LUMO)	14.3%
						(HOMO-12)→(LUMO)	11.8%
						(HOMO-2)→(LUMO+2)	12.3%
	302.1	0.55	303.0	0.96	$S_0 \rightarrow S_{66}$	(HOMO-12)→(LUMO)	14.5%

In order to clearly demonstrate the space relationship between the Gn

moiety and the porphyrin fragment of the studied hybrid molecules, the torsion angle between the two parts is drawn in Fig.S1.

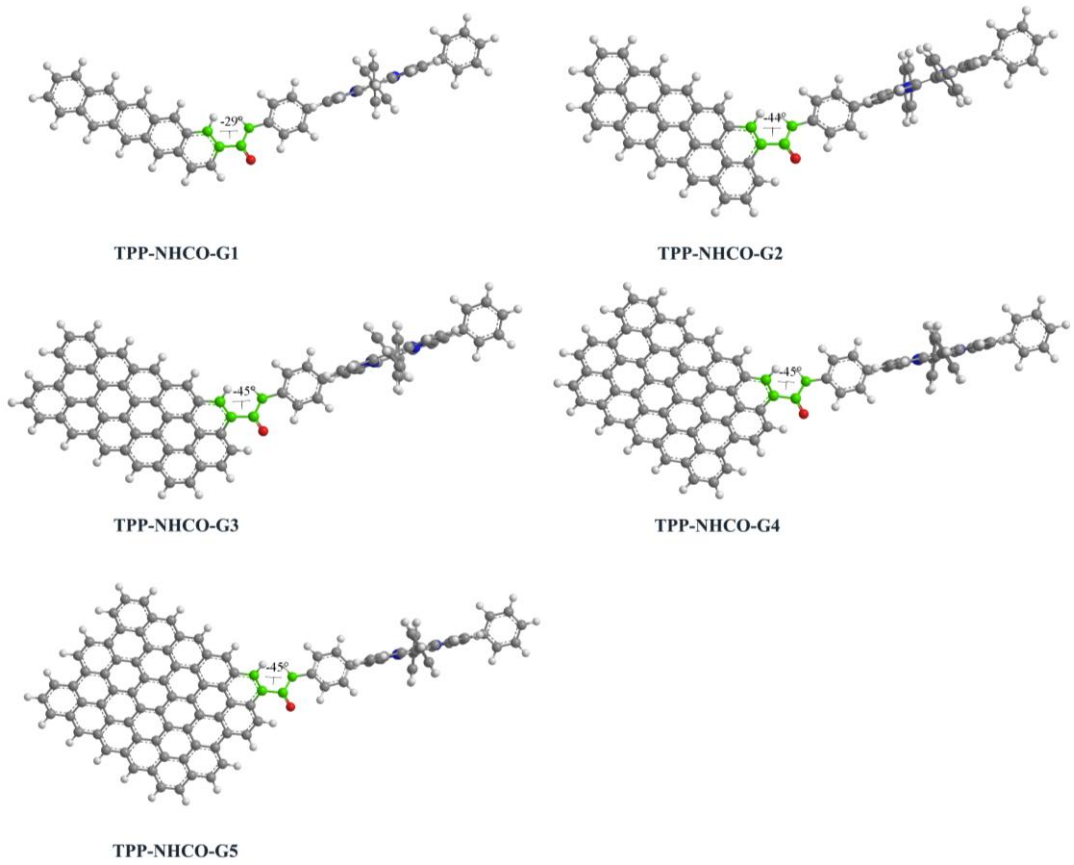
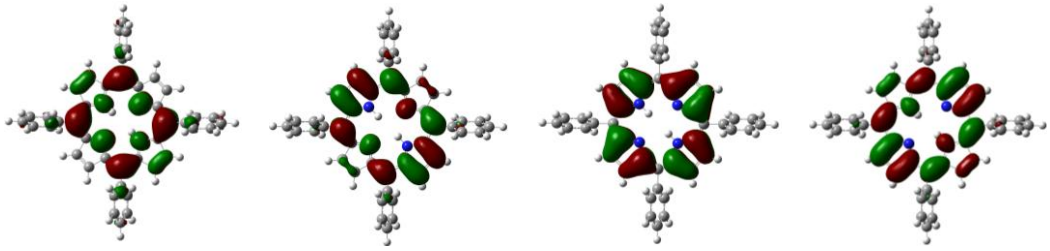


Fig.S1. The torsion angle between the Gn moiety and the porphyrin fragment of the studied hybrid molecules.

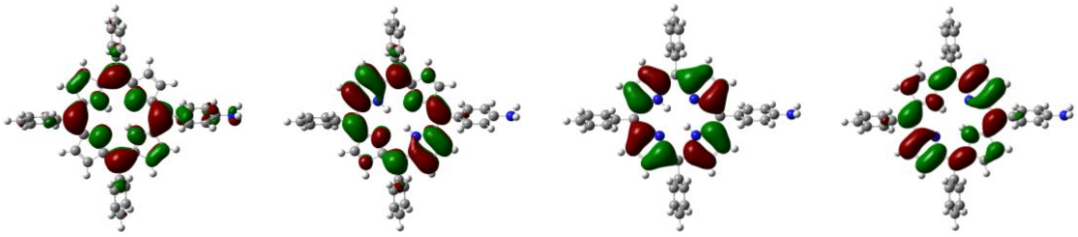
To better understand the the transition features of the OPA and TPA properties, the relevant frontier molecular orbitals of all the studied molecules are listed in Fig.S2.

TPP



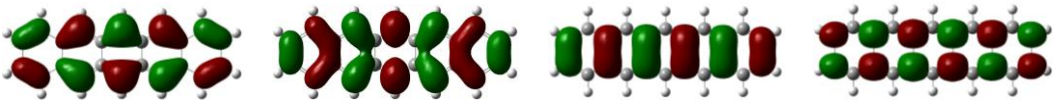
HOMO LUMO HOMO-1 LUMO+1

TPP-NH_2



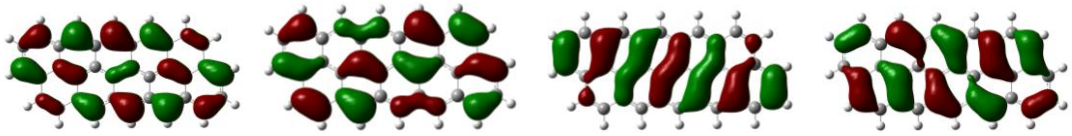
HOMO LUMO HOMO-1 LUMO+1

G1

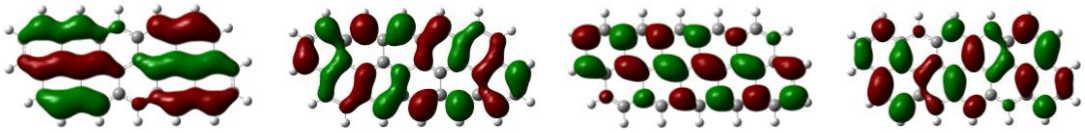


HOMO LUMO HOMO-2 LUMO+2

G2

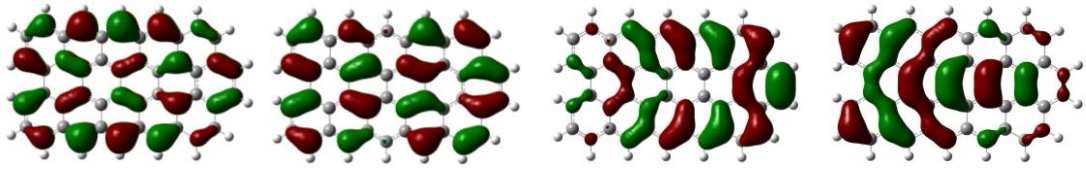


HOMO HOMO-1 HOMO-2 HOMO-4

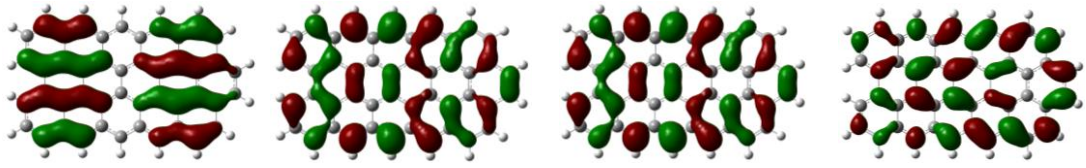


HOMO-6 LUMO LUMO+2 LUMO+4

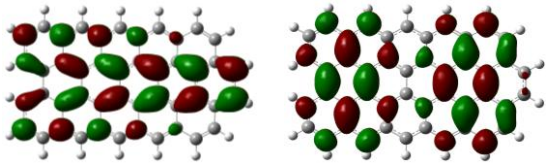
G3



HOMO HOMO-1 HOMO-2 HOMO-3

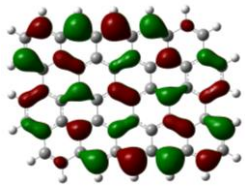


HOMO-7 LUMO LUMO+1 LUMO+2

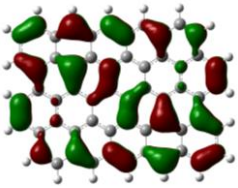


LUMO+3 LUMO+6

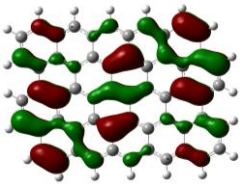
G4



HOMO



HOMO-2



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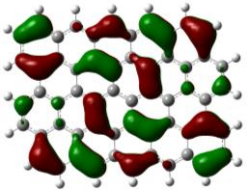

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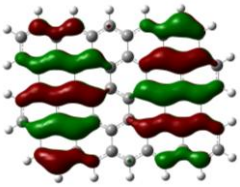
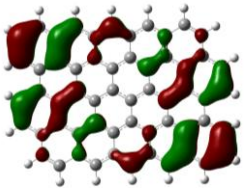


HOMO-7



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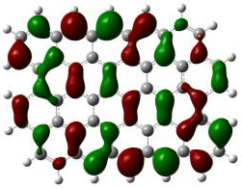
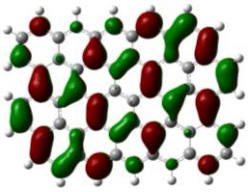


LUMO



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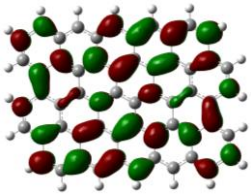

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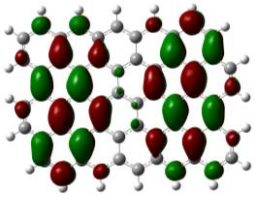

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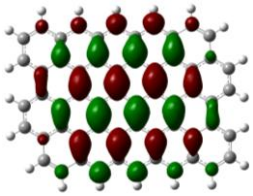
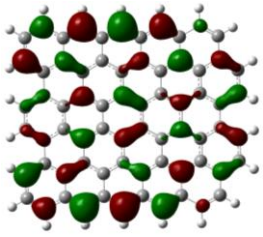
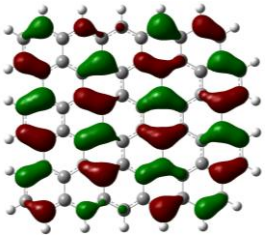


LUMO+9

G5



HOMO



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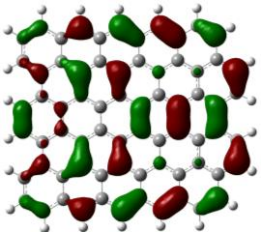

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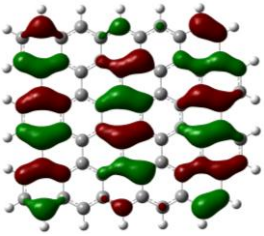

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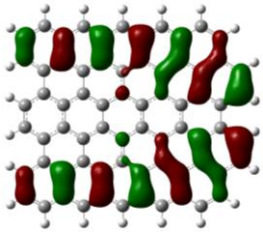

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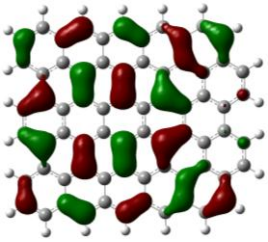

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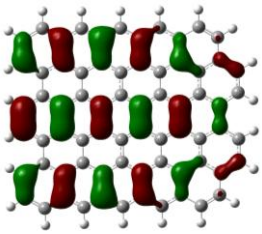

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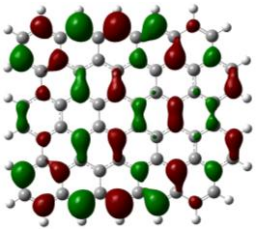
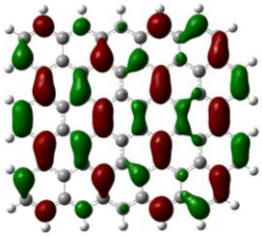


LUMO



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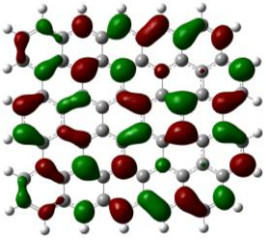

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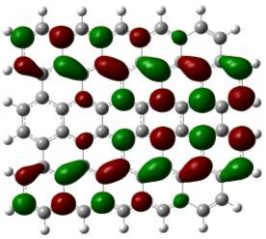
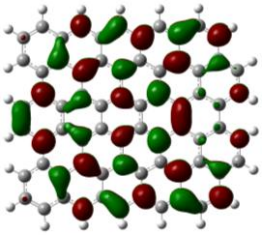
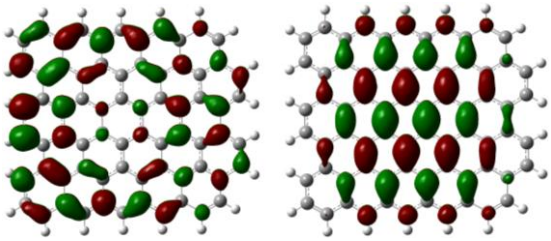


LUMO+5

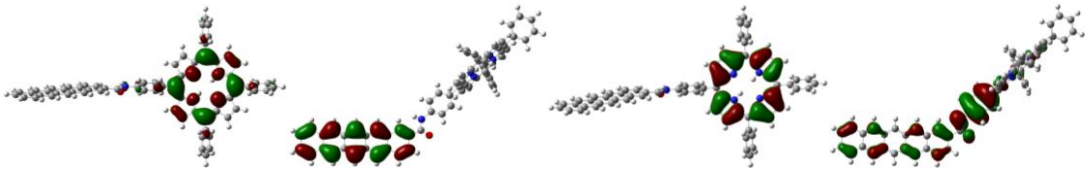


LUMO+7

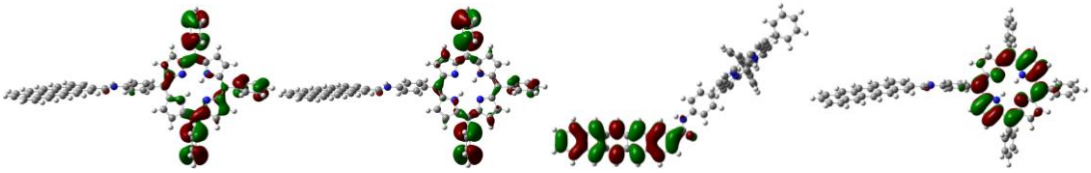


LUMO+8 LUMO+10

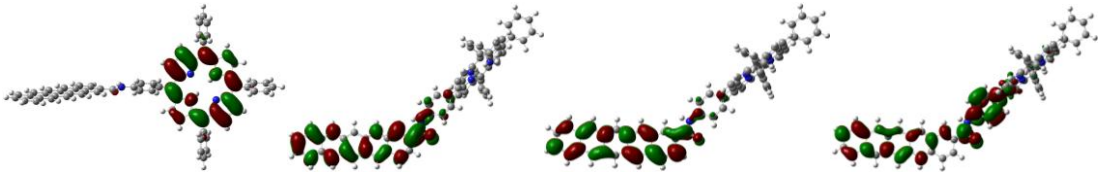
TPP-NHCO-G1



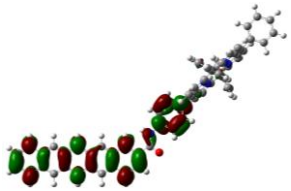
HOMO HOMO-1 HOMO-2 HOMO-3



HOMO-8 HOMO-10 LUMO LUMO+1

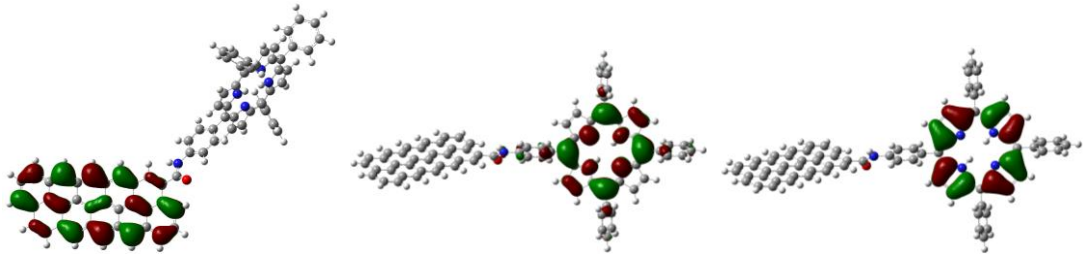


LUMO+2 LUMO+3 LUMO+4 LUMO+6

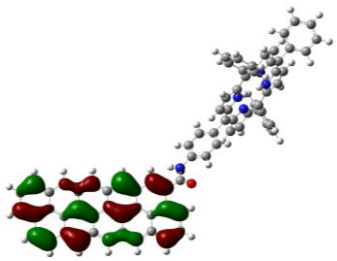


LUMO+14

TPP-NHCO-G2



HOMO HOMO-1 HOMO-2



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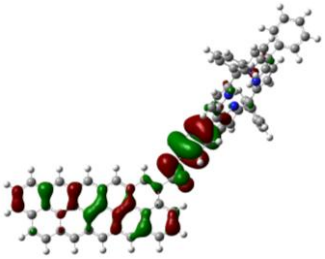

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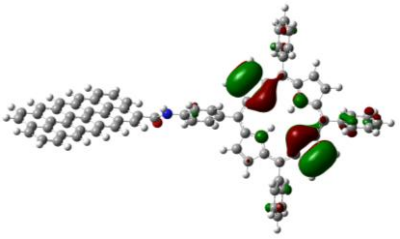
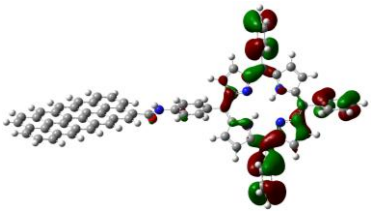
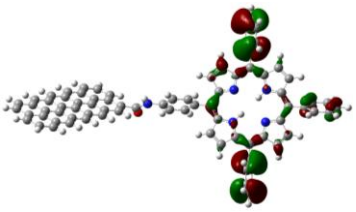


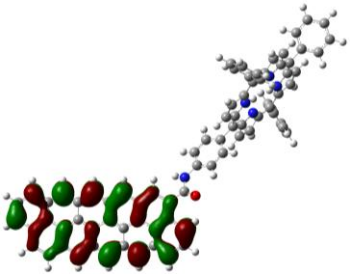
HOMO-7



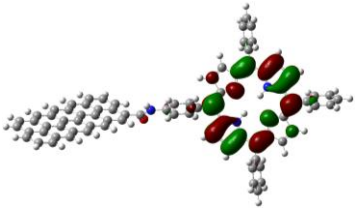
HOMO-10



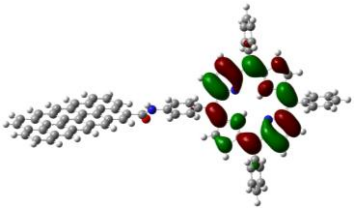
HOMO-12



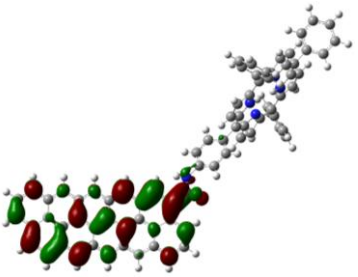
LUMO



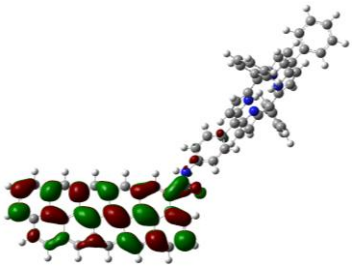
LUMO+1



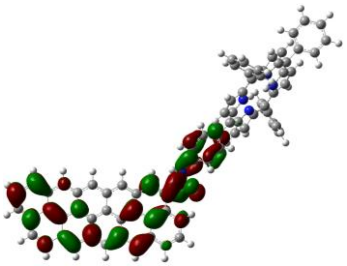
LUMO+2



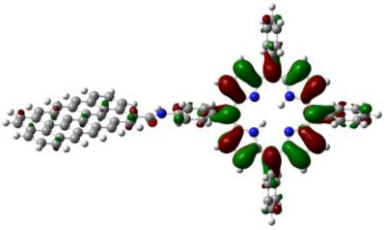
LUMO+3



LUMO+4

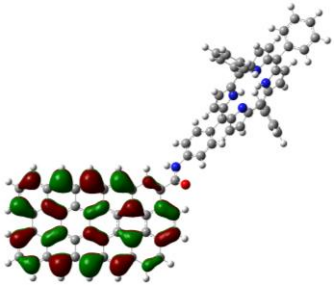


LUMO+5

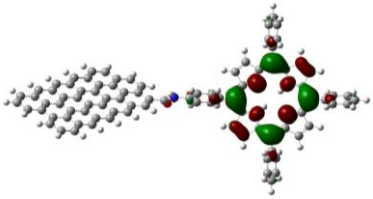


LUMO+7

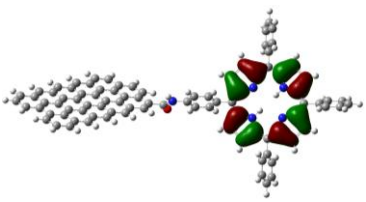
TPP-NHCO-G3



HOMO



HOMO-1



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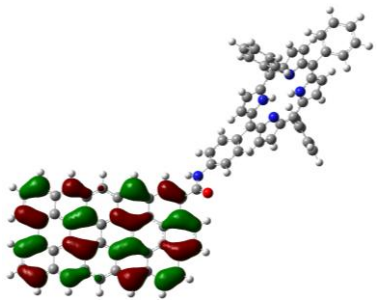

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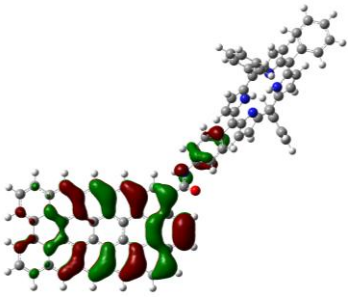
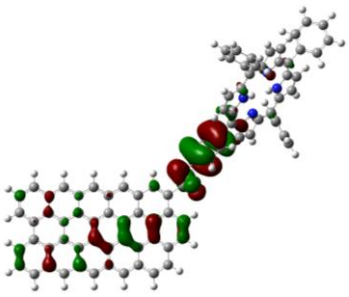
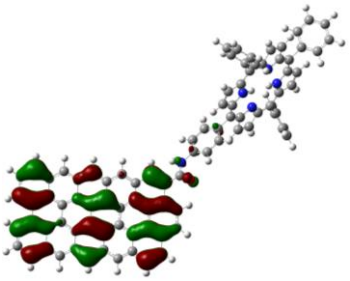


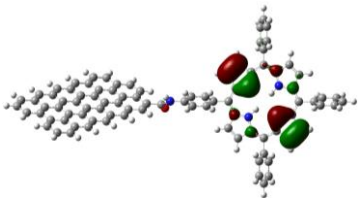
HOMO-4



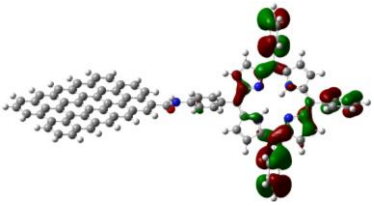
HOMO-5



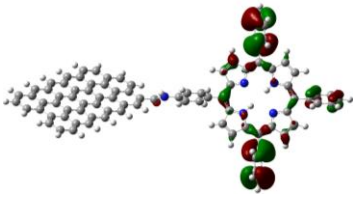
HOMO-7



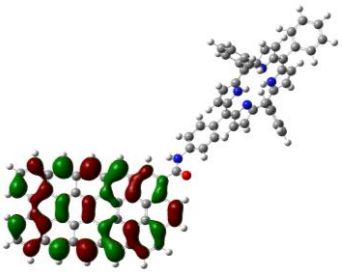
HOMO-8



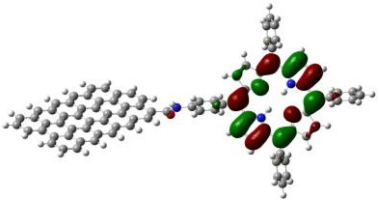
HOMO-11



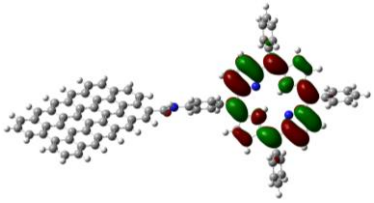
HOMO-13



LUMO



LUMO+1



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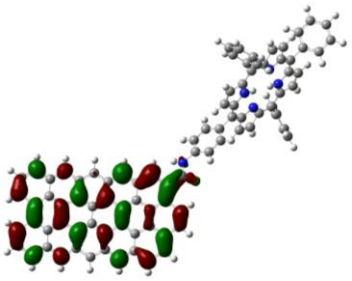

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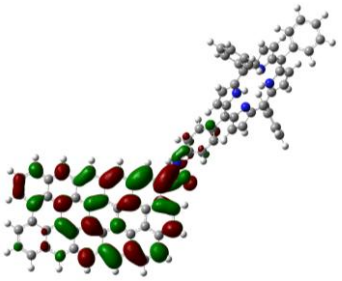

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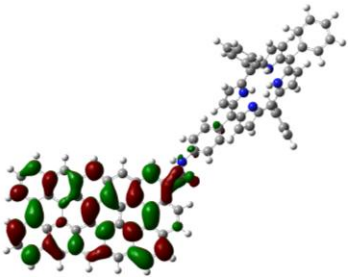

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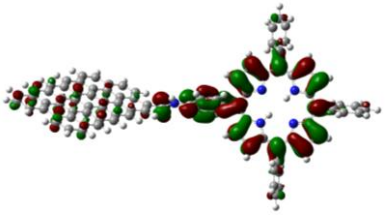

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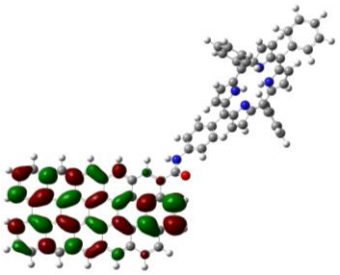

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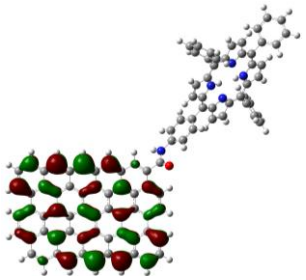

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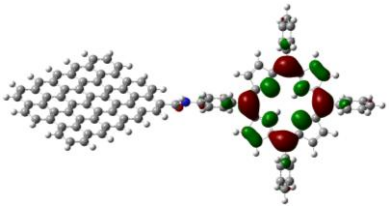

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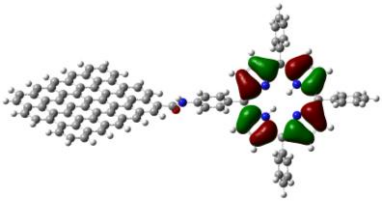

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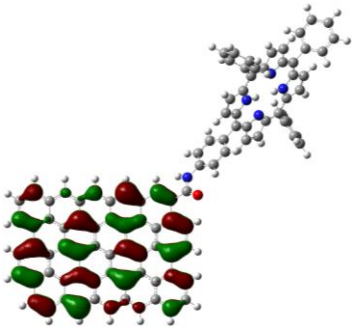

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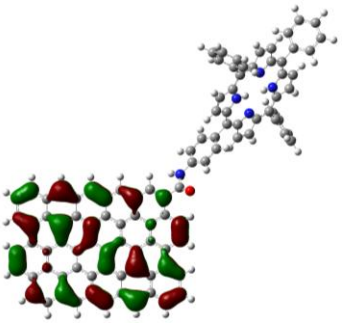

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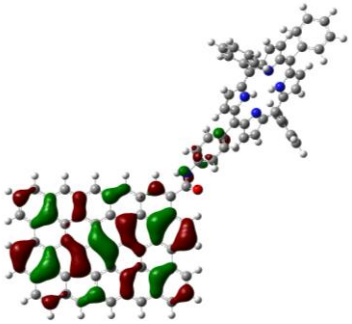

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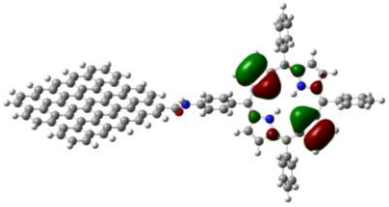

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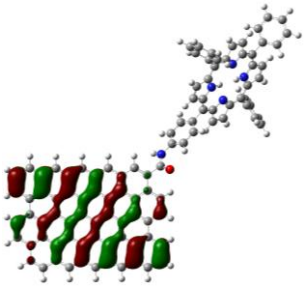

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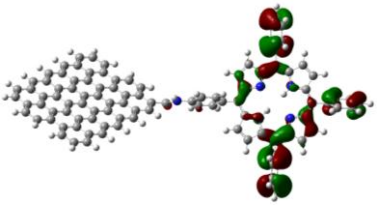

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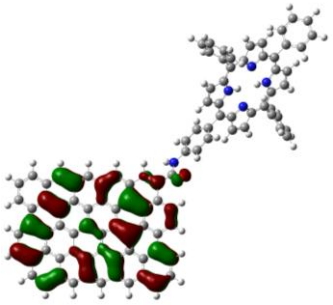

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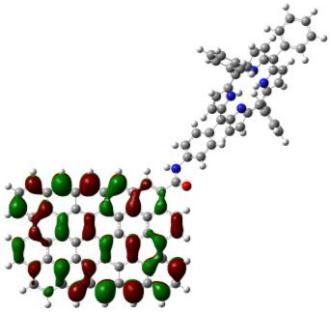

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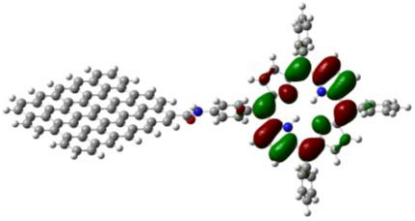

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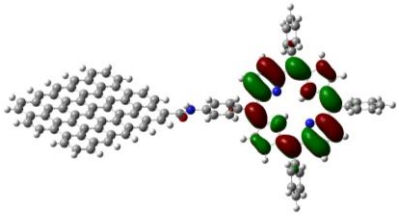

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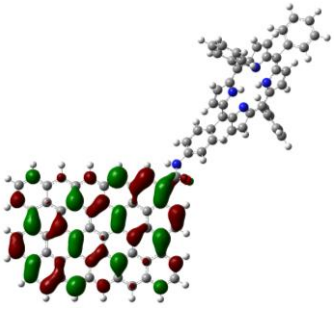

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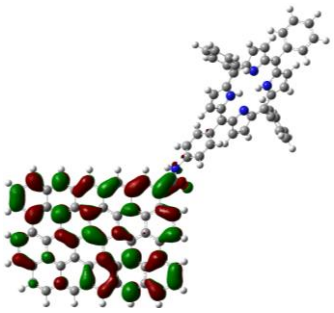

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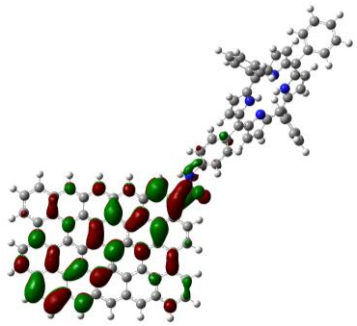

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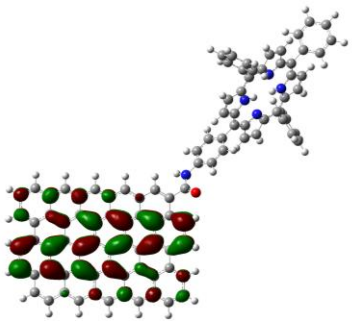

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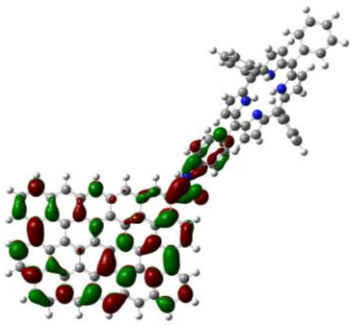

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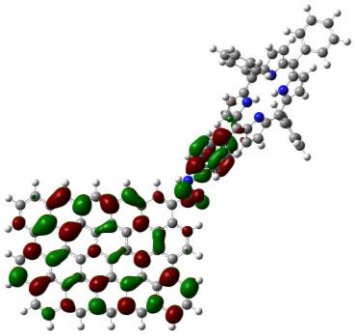

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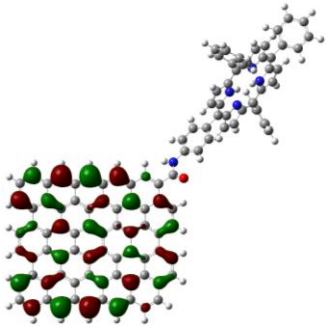
TPP-NHCO-G5



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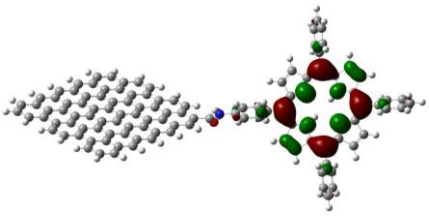

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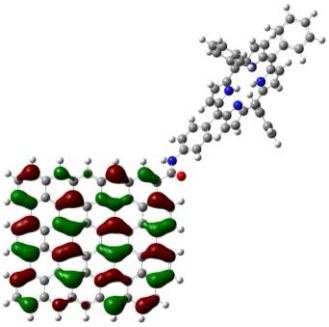

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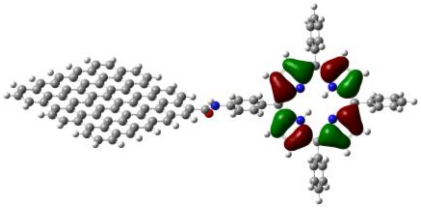

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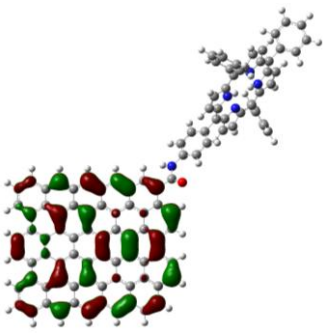

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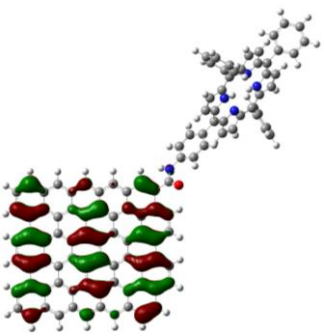

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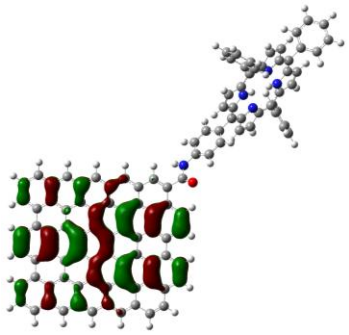

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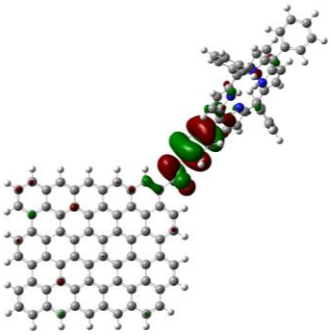

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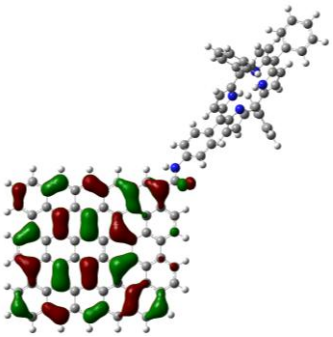

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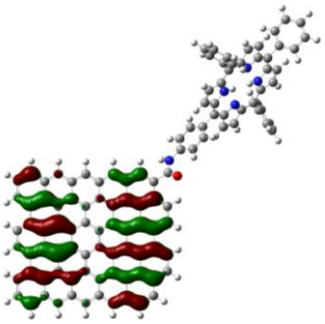

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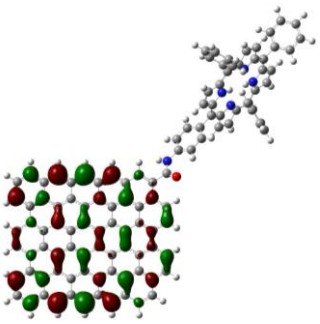

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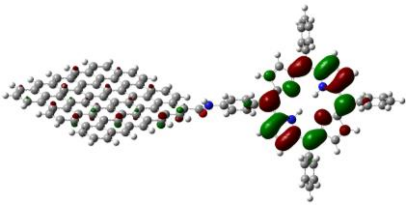

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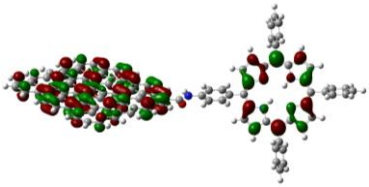

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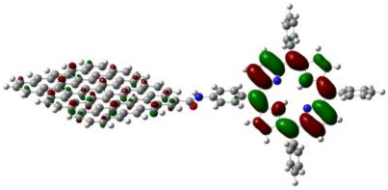

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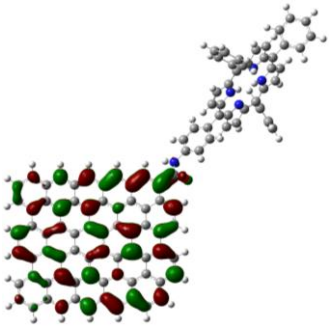

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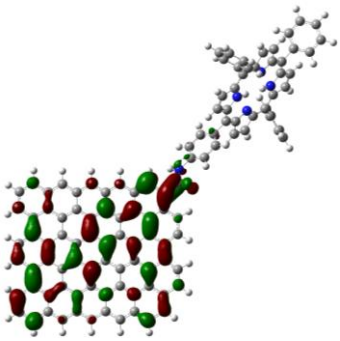

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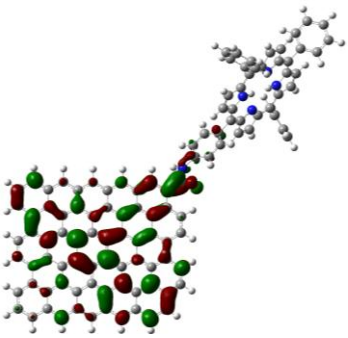

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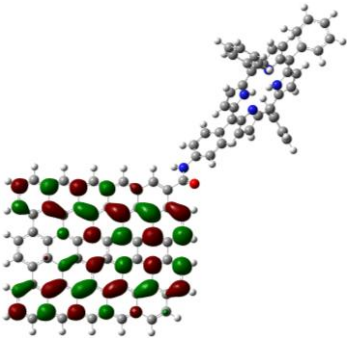

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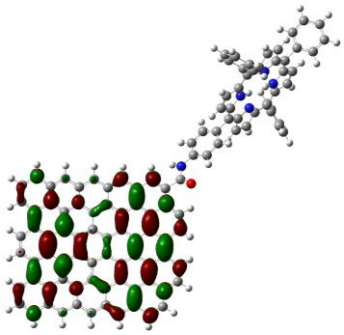


LUMO+11

Fig.S2. Contour surfaces of the frontier molecular orbitals of all the studied molecules.

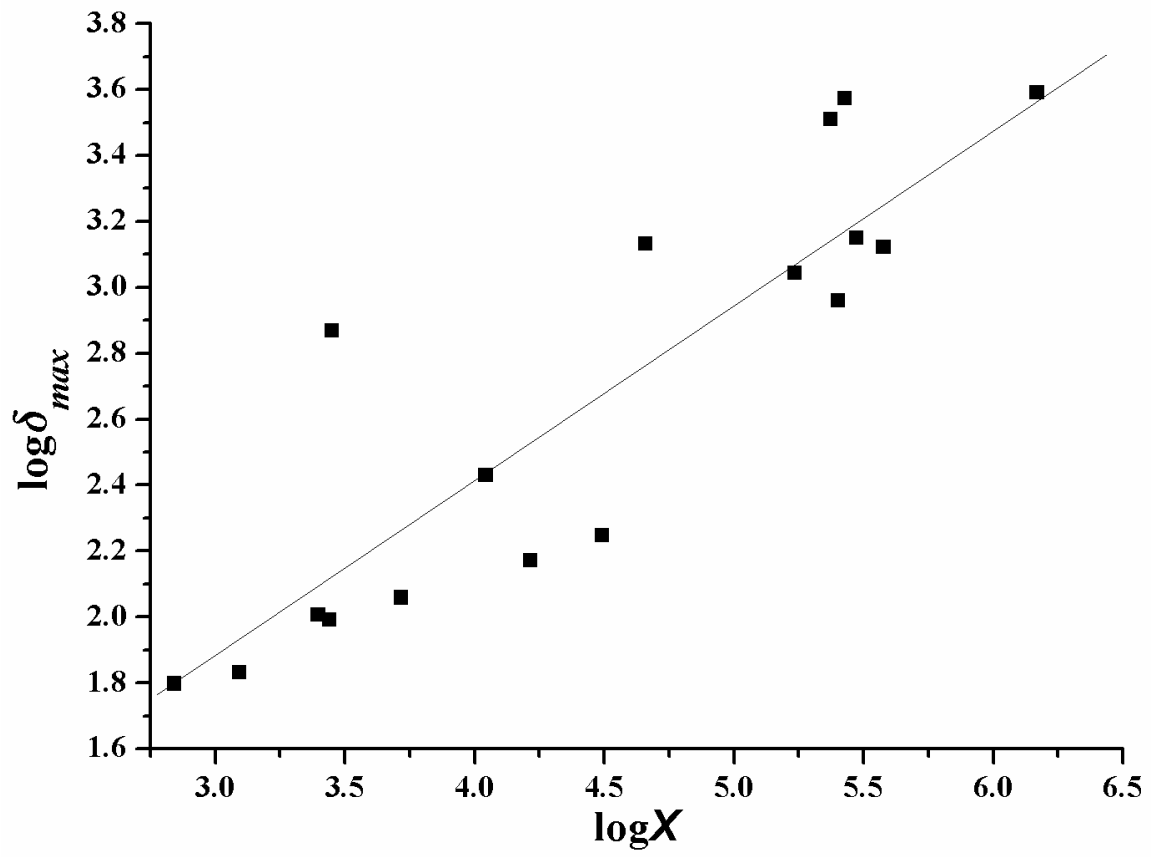
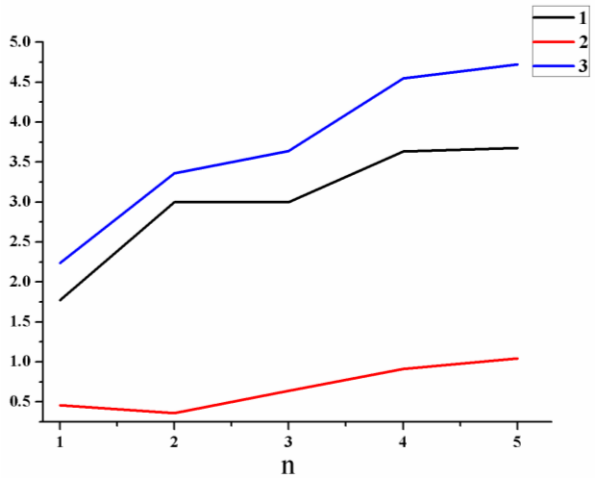


Fig.S3. The Plot of logδ_{max} versus log$X$

In order to more intuitively observe which factor has a greater impact on the δ_{max} values, the relationships of the impact factors (1-3) versus repeat unit number n are shown in Fig.S4.

1 represents $\log M_{0k}^2 M_{kn}^2$, 2 represents $\log\left[1/\left(E_{0k}-E_{0n}/2\right)^2\right]$, 3 represents $\log(X\Gamma)$ in Fig.S4. **n** refers to the unit repeat number in Gn and TPP-NHCO-Gn (n=1-5).

A)



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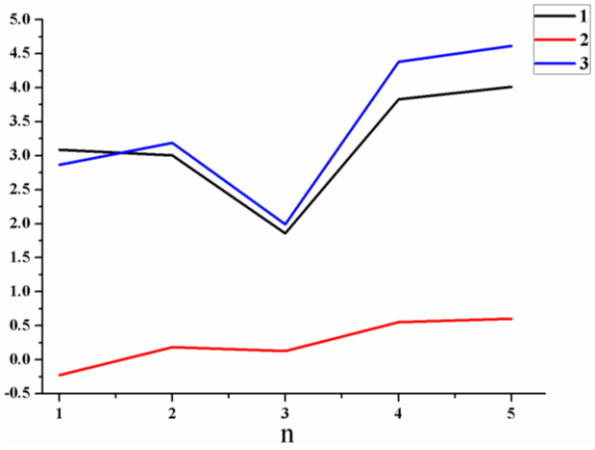

C)

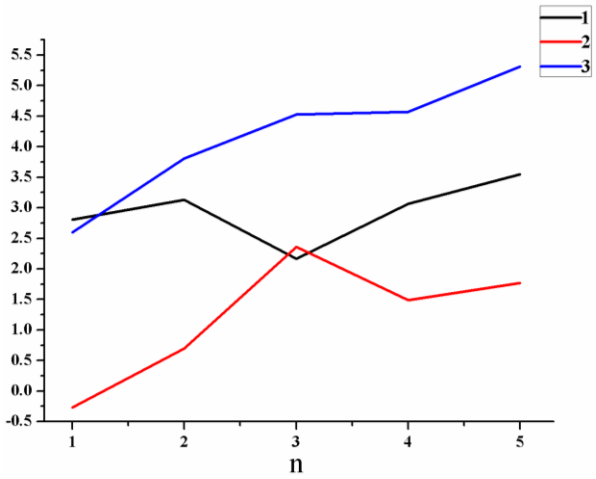

Fig.S4. The relationships of the impact factors $\log M_{0k}^2 M_{kn}^2$ (1), $\log\left[1/\left(E_{0k}-E_{0n}/2\right)^2\right]$ (2) and $\log(X\Gamma)$ (3) versus **n**

A) represents the proportion relationships of $\log M_{0k}^2 M_{kn}^2$ (curve 1), $\log\left[1/\left(E_{0k}-E_{0n}/2\right)^2\right]$ (curve 2) and $\log(X\Gamma)$ (curve 3) versus unit number **n** in Gn molecules.

B) represents the proportion relationships of $\log M_{0k}^2 M_{kn}^2$ (curve 1), $\log\left[1/\left(E_{0k}-E_{0n}/2\right)^2\right]$ (curve 2) and $\log(X\Gamma)$ (curve 3) of the first TPA peaks in hybrid molecules versus unit number **n**.

C) represents the proportion relationships of $\log M_{0k}^2 M_{kn}^2$ (curve 1), $\log\left[1/\left(E_{0k}-E_{0n}/2\right)^2\right]$ (curve 2) and $\log(X\Gamma)$ (curve 3) of the second TPA peaks versus unit number **n** in hybrid molecules.