Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Novel *s*-tetrazine-based dyes with enhanced two-photon absorption cross-sections

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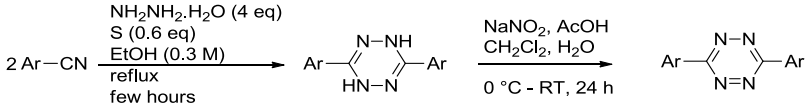
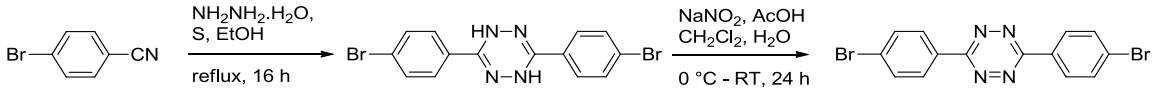
General procedure for Pinner reaction and oxidation



To a solution of nitrile (1.0 eq) in ethanol (0.3 M) were added monohydrate hydrazine (4.0 eq) and sulfur (0.6 eq). The mixture was refluxed until complete reaction as judged by TLC. All volatile substances were removed by concentration under reduced pressure to give a yellow solid used without further purification. The yellow solid (1 eq) was dissolved in dichloromethane (0.3 M). A solution of sodium nitrite (6 eq) in water (0.3 M) was added. Acetic acid (5 eq) was added dropwise at 0 °C. The mixture was stirred at room temperature until complete reaction as judged by TLC. Organic compounds were extracted with dichloromethane. The combined organic phases were dried over anhydrous sodium sulfate, filtrated and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography to give a pink or red powder.

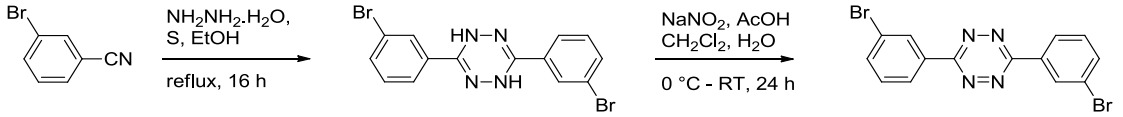
3,6–bis(4'-bromophenyl)-*s*-tetrazine



General procedure for Pinner reaction and oxidation with 4-bromobenzonitrile (1.8 g, 10.0 mmol).

Chromatography conditions: CH_2Cl_2; Yield: 35% (686 mg); mp: > 260 °C (lit.,[1,2] 290-292 and 337 °C); IR (ν_{max}/cm^{-1}): 1587, 1406, 1392, 1105, 1068, 1006, 915, 836, 825; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (d, J=8.7 Hz, 4H); 7.64 (d, J=8.7 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.4; 132.7; 129.4; 129.0; 125.9; UV-vis (CH_2Cl_2): λ_{max}=314 and 547 nm

3,6-bis(3'-bromophenyl)-*s*-tetrazine

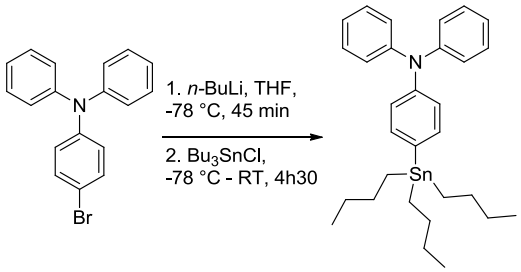


General procedure for Pinner reaction and oxidation with 3-bromobenzonitrile (1.8 g, 9.9 mmol).

Chromatography conditions: CH_2Cl_2/Petroleum Ether(PE): 5/5; Yield: 74% (1.43 g); mp: 244 °C; IR (ν_{max}/cm^{-1}): 1433, 1381, 1299, 1091, 1056, 922, 888, 795, 767, 738, 686, 679; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.83 (dd, J=1.8 and 1.8 Hz, 2H), 8.60 (ddd, J=7.8, 1.8 and 0.9 Hz, 2H), 7.79 (ddd, J=7.8, 1.8 and 0.9 Hz, 2H), 7.51 (dd, J=7.8 and 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.4, 136.0, 133.7, 131.1, 131.0, 126.7, 123.7; HRMS-MALDI (m/z):

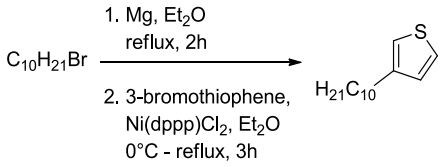
$(M+H)^+$ calcd for $C_{14}H_8Br_2N_4$, 392.9173 (100%), 390.9194 (51%), 394.9153 (49%), found: 392.9184 (100%), 390.9187 (52%), 394.9172 (48%); UV-vis (CH_2Cl_2): λ_{max}=294 and 547 nm

Synthesis of *N,N*-diphenyl-4-tributyltinaniline



1.6 M solution of *n*BuLi in hexane (3.4 mL, 5.4 mmol, 1.0 eq) was added dropwise to a solution of 4-bromo-*N,N*-triphenylamine (1.8 g, 5.4 mmol, 1.0 eq) in THF (48 mL) at -78°C and stirred for 45min at this temperature. Bu_3SnCl (1.6 mL, 5.7 mmol, 1.1 eq) was added and the reaction mixture was stirred for 4h30 at room temperature under argon. After removing all volatile materials under reduced pressure *N,N*-diphenyl-4-tributyltinaniline was obtained as colorless oil (1.4 g, 2.7 mmol, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32 (d, J=8.2 Hz, 2H) ; 7.25 (dd, J=8.7 and 7.3 Hz, 4H), 7.11 (dd, J=7.3 and 1.5 Hz, 4H), 7.04 (d, J=8.7 Hz, 2H), 7.01 (t, J=7.3 Hz, 2H), 1.60-1.50 (m, 6H), 1.38-1.29 (m, 6H), 1.05-1.00 (m, 6H), 0.89 (t, J=7.3 Hz, 9H)

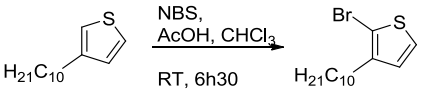
3-decylthiophene



1-bromodecane (5.8 mL, 37 mmol, 1.7 eq) was added dropwise to a solution of iodine (60 mg, 0.24 mmol, 0.01 eq) and magnesium (0.92 g, 38 mmol, 1.7 eq) in diethylether (30 mL). The reaction mixture was refluxed for 2 hours under argon and then cooled down to room temperature. This solution was added at 0°C to a solution of 3-bromothiophene (2.0 mL, 21 mmol, 1.0 eq) and dichloro(1,3-bis(diphenylphosphino)propane)nickel (135 mg, 0.25 mmol, 0.01 eq) in diethylether (20 mL). The reaction mixture was refluxed for 16 hours under argon and then cooled down to room temperature. Water (50 mL) was added and organic compounds were extracted with diethylether (5*100 mL). The combined organic phases were washed with saturated sodium chloride solution (300 mL), dried over anhydrous sodium sulfate, filtrated and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (hexane) to give a colorless liquid. Yield: 96% (4.61g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.21 (m, 1H), 6.92-6.90 (m, 2H), 2.60 (t, J=7.8 Hz, 2H), 1.59 (tt, J=7.8 and 6.9

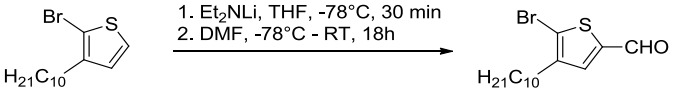
Hz, 2H), 1.30-1.15 (m, 14H), 0.86 (t, J=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.4, 128.4, 125.2, 119.9, 32.1, 30.7, 30.4, 29.9, 29.78, 29.77, 29.6, 29.5, 22.9, 14.3

2-bromo-3-decylthiophene



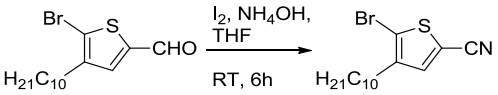
To a solution of 3-decylthiophene (2.0 g, 8.9 mmol, 1.0 eq) in a mixture of solvents acetic acid/chloroform (1/1, 30 mL) was portionwise added *N*-bromosuccinimide (1.6 g, 8.9 mmol, 1.0 eq) at 0 °C and without light. The reaction mixture was stirred at room temperature for 17 hours before being poured into iced water (100 mL). Organic compounds were extracted with chloroform (5*100 mL). The combined organic phases were washed with water (2*200 mL) and saturated sodium chloride solution (200 mL), dried over anhydrous sodium sulfate, filtrated and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (hexane) to give a colorless liquid. Yield: 69% (1.9 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (d, J=5.6 Hz, 1H), 6.77 (d, J=5.6 Hz, 1H), 2.54 (t, J=7.6 Hz, 2H), 1.55 (tt, J=7.6 and 7.6 Hz, 2H), 1.30-1.25 (m, 14H), 0.86 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.1, 128.4, 125.3, 108.4, 32.1, 29.9, 29.8, 29.7, 29.6, 29.54, 29.48, 29.4, 22.8, 14.3.

5-bromo-4-decylthiophene-2-carboxaldehyde



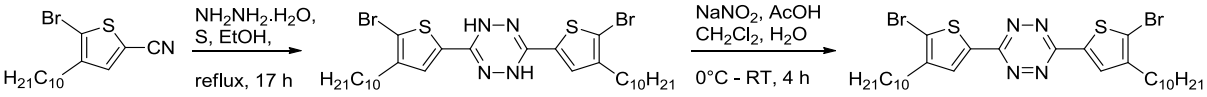
At -78 °C under argon, to THF (12 mL) was added first Et_2NLi (1.0 g, 13 mmol, 2.1 eq) and then 2-bromo-3-decylthiophene (1.9 g, 6.1 mmol, 1.0 eq). The reaction mixture was stirred at -78 °C for 30 minutes before dimethylformamide (2.4 mL, 31 mmol, 5.1 eq) was added. The reaction mixture was stirred for 18 hours from -78 °C to room temperature. 1 M hydrochloric acid (120 mL) was added and organic compounds were extracted with ethyl acetate (3*100 mL). The combined organic phases were washed with saturated sodium chloride solution (250 mL), dried over anhydrous magnesium sulfate, filtrated and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (CH_2Cl_2/PE) to give a colorless liquid. Yield: 70% (1.4 g). IR (ν_{max}/cm^{-1}): 2971, 2921, 1669, 1427, 1407, 1394, 1377, 1233, 1150, 1066, 1057, 1028, 892, 879, 868; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.75 (s, 1H), 7.48 (s, 1H), 2.59 (t, J=7.4 Hz, 2H), 1.61 (tt, J=7.4 and 7.4 Hz, 2H), 1.5-1.2 (m, 14H), 0.88 (t, J=6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 181.7, 143.9, 142.9, 136.7, 121.9, 31.9, 29.6, 29.6, 29.5, 29.4, 29.34, 29.32, 29.1, 22.7, 14.1

5-bromo-4-decylthiophene-2-carbonitrile



33% Ammoniacal solution (42 mL) was added to a solution of 5-bromo-4-decylthiophene-2-carboxaldehyde (0.83 g, 2.5 mmol, 1.0 eq) in THF (8 mL). Iodine (1.3 g, 5.0 mmol, 2.0 eq) was then added. Mixture was stirred at room temperature for 3 hours. 5% Sodium thiosulfate solution (20 mL) was then added. Organic compounds were extracted with ethyl acetate (3*30 mL). The combined organic phases were dried over anhydrous sodium sulfate, filtrated and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (CH_2Cl_2/PE: 3/7) to give a colorless oil. Yield: 87% (0.72 g). IR (ν_{max}/cm^{-1}): 2950, 2912, 2850, 2217, 1552, 1454, 1437, 1394, 1182, 1069, 910, 852, 837; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (s, 1H), 2.55 (t, J=7.6 Hz, 2H), 1.56 (tt, J=7.3 and 7.3 Hz, 2H), 1.32-1.22 (m, 14H), 0.81 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.2, 138.0, 116.7, 113.4, 109.4, 31.8, 29.5, 29.4, 29.3, 29.2 (2C), 29.1, 29.0, 22.6, 14.1

3,6-bis(5-bromo-4-decylthiophen-2-yl)-*s*-tetrazine



General procedure for Pinner reaction and oxidation with 5-bromo-4-decylthiophene-2-carbonitrile (0.75 g, 2.3 mmol).

Chromatography conditions: CH_2Cl_2/PE:8/2; Yield: 65% (0.51 g); mp: 83 °C; IR (ν_{max}/cm^{-1}): 2950, 2911, 2849, 1551, 1471, 1454, 1437, 1394, 1372, 1264, 1182, 1069, 910, 852, 837; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (s, 2H), 2.63 (t, J=7.6 Hz, 4H), 1.65 (tt, J=7.5 and 7.5 Hz, 4H), 1.34-1.27 (m, 28H), 0.88 (t, J=6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.8, 144.8, 135.1, 131.6, 118.1, 32.0, 29.8, 29.74, 29.70, 29.6, 29.52, 29.47, 29.3, 22.8, 14.3; HRMS-EI (m/z): $(M)^{\bullet+}$ calcd for $C_{30}H_{44}{}^{79}BrN_4S_2$, 682.1374, found: 682.1379

(1) Liu, H.; Wei, Y. *Tetrahedron Lett.* **2013**, *54*, 4645.
(2) Scott, F. L.; O'Halloran, J. K.; O'Driscoll, J.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2224.

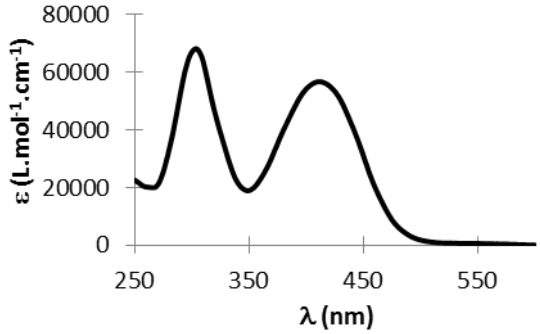


Figure S 1. Molar absorption coefficient of compound 1 in dichloromethane

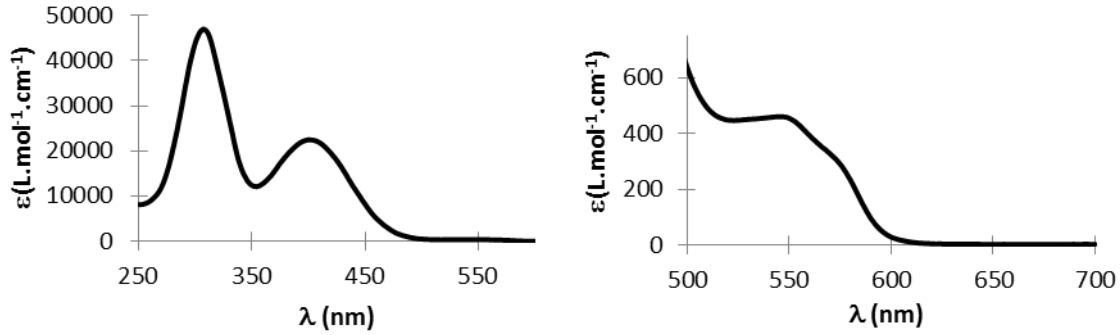


Figure S 2. Molar absorption coefficient of compound 2 in dichloromethane

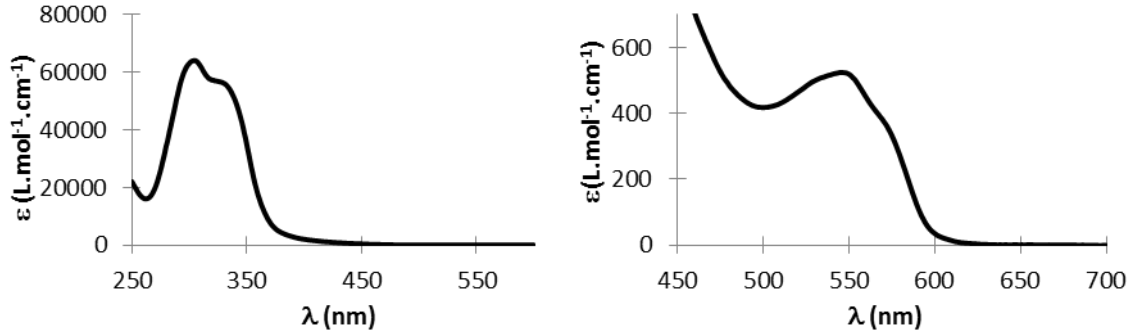


Figure S 3. Molar absorption coefficient of compound 3 in dichloromethane

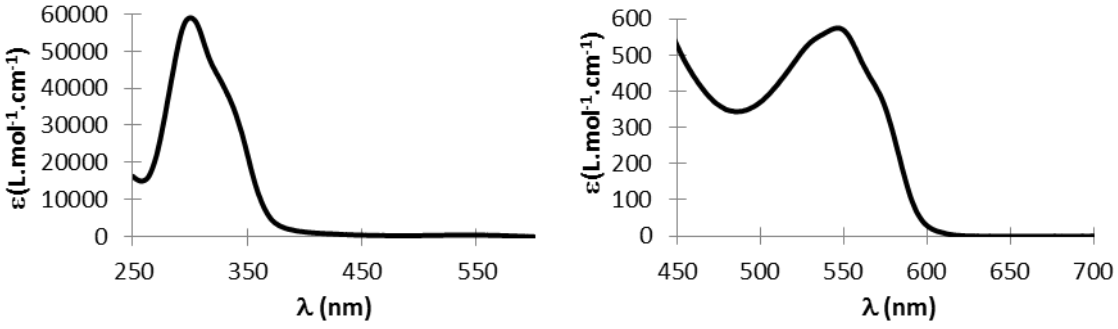


Figure S 4. Molar absorption coefficient of compound 4 in dichloromethane

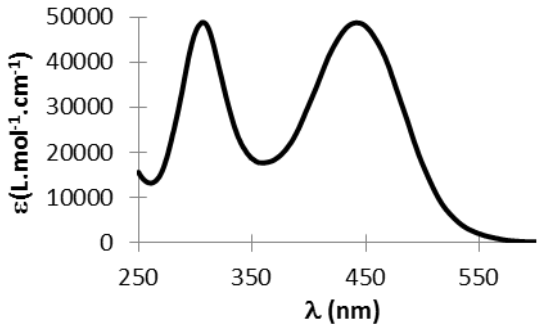


Figure S 5. Molar absorption coefficient of compound 5 in dichloromethane

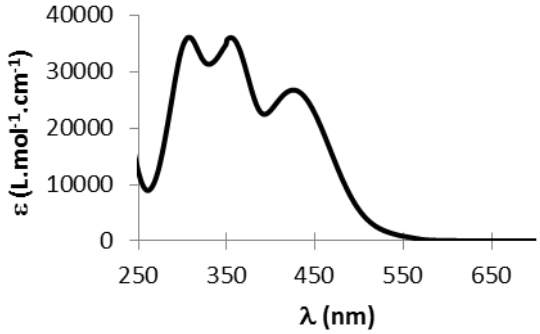


Figure S 6. Molar absorption coefficient of compound 6 in dichloromethane

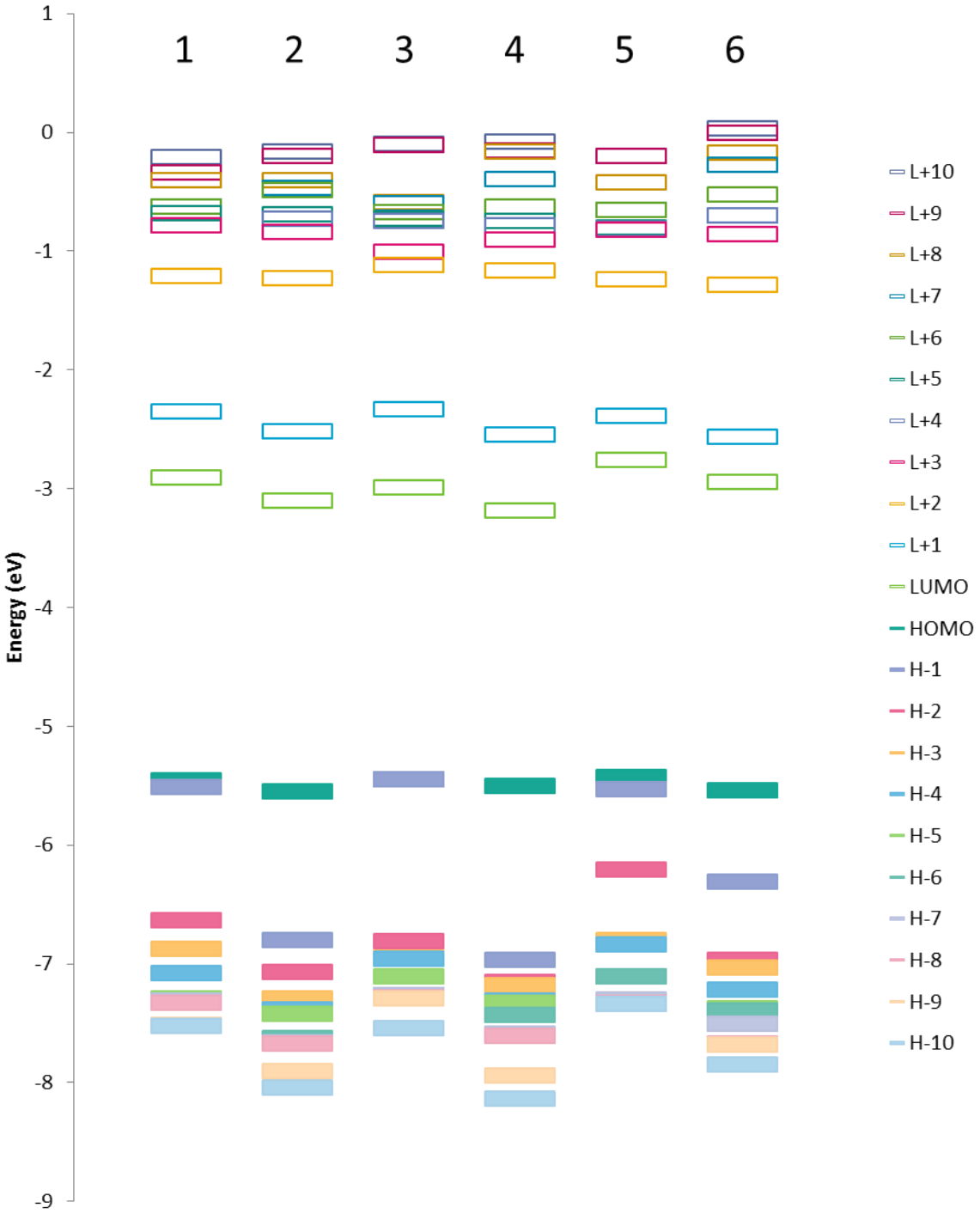


Figure S 7. Energy levels of the orbitals H-10 to L+10 for the compounds 1-6

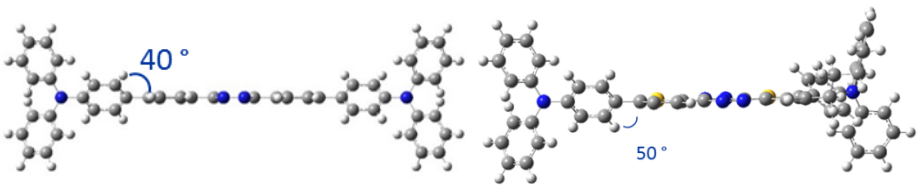


Figure S 8. Geometry of the compound 1 (left) and 5 (right). The value of the dihedral angle between the link (phenylene for 1 and thiophenylene for 5) and the phenylene of the triphenylamine is indicated.

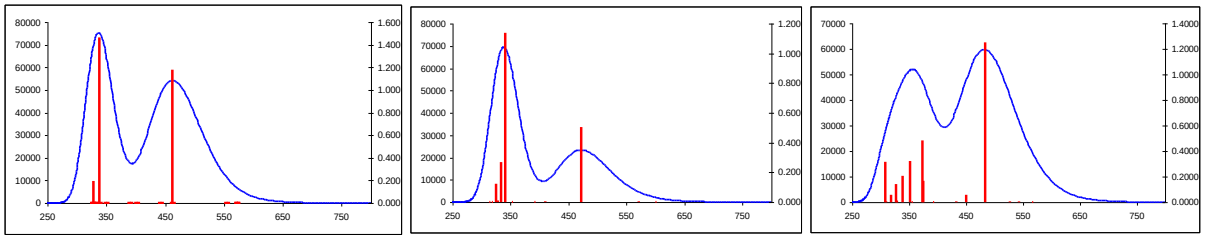


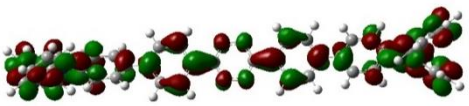
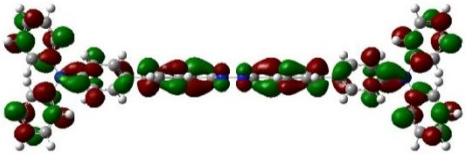
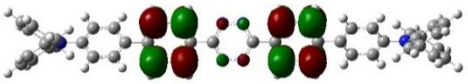
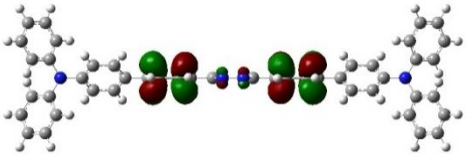
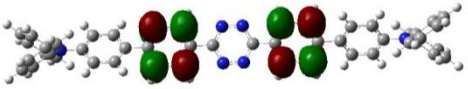
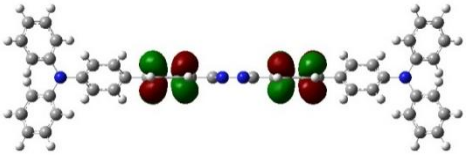
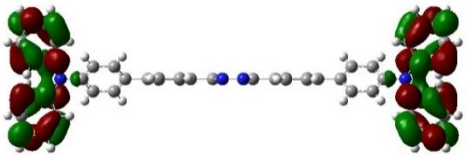
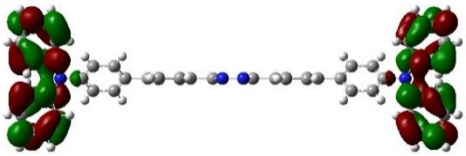
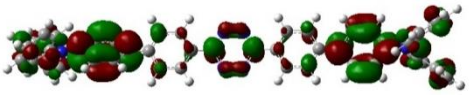
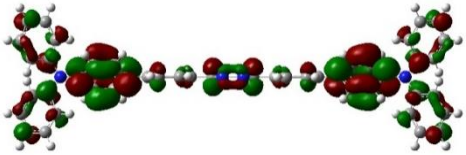
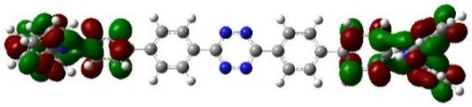
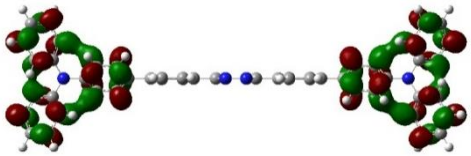
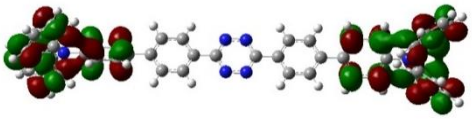
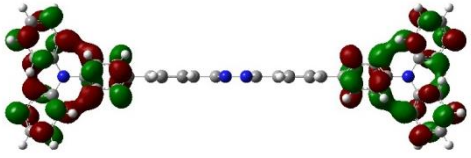
Figure S 9. Calculated spectra for compounds 1 (left), 2 (middle) and 5 (right) - Calculated spectra have been obtained using a Gaussian with a FWHM of 4750cm-1 (0.59 eV) and a surface equal to the calculated oscillator strength. Red lines indicate the position of the calculated vertical transitions. Their height is equal to the calculated oscillator strength.

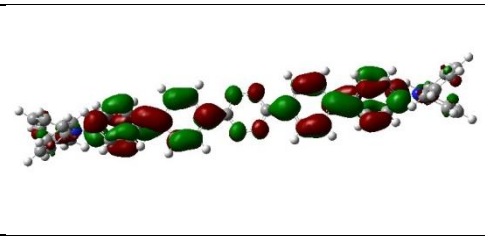
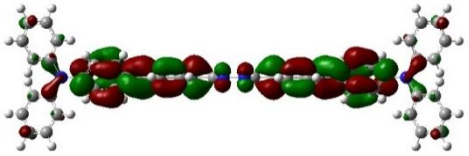
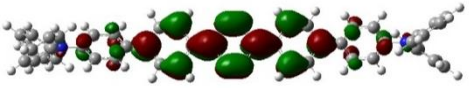
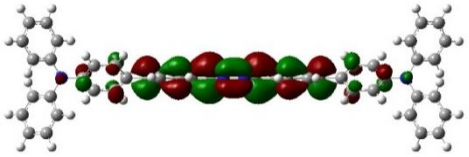
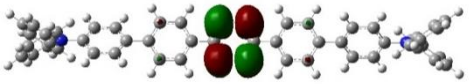
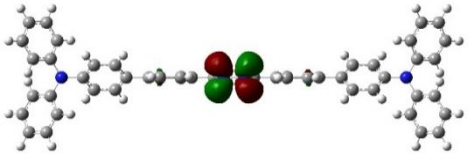
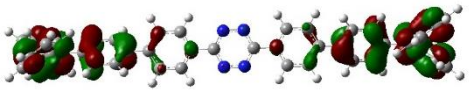
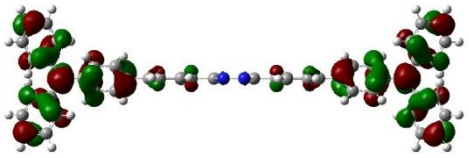
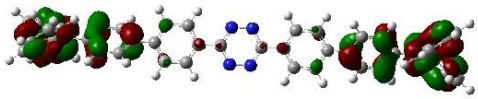
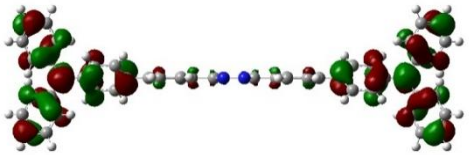
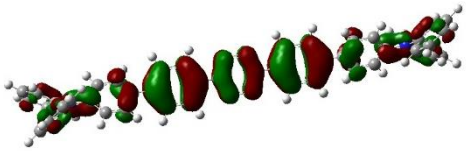
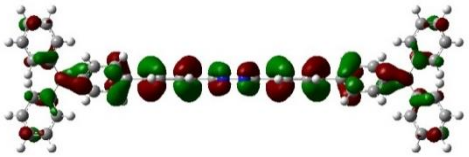
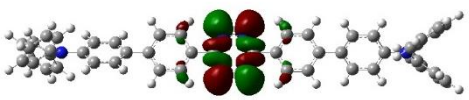
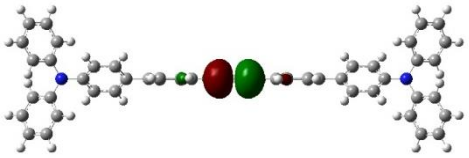
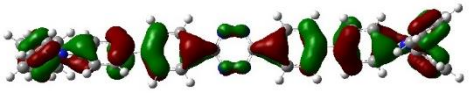
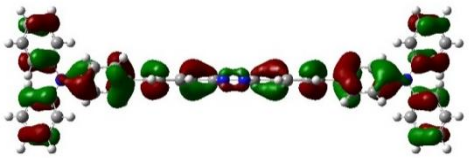
Table S 1. Main results of TD-DFT calculations

Compound	Energy (cm^{-1})	Energy (nm)	Oscillator strength	Major contributing molecular orbitals
1	17481	572	0.003	H-3→LUMO (80%)
	18049	554	0.0002	H-1->LUMO (93%)
	21628	462	1.18	HOMO→L+1 (94%)
	29626	338	1.46	H-2→L+1 (59%), H-1→L+2 (22%)
2	16668	600	0.0002	HOMO->LUMO (97%)
	17531	570	0.003	H-2→LUMO (84%)
	21203	472	0.51	HOMO→L+1 (95%)
	29409	340	1.14	H-1→L+1 (55%), HOMO→L+2 (22%)
3	17506	571	0.003	H-4→LUMO (47%), H-3→LUMO (38%)
	29111	344	1.72	H-2→L+1 (10%), H-1→L+2 (43%), HOMO→L+3 (32%)
4	17550	570	0.003	H-2→LUMO (85%)
	31355	341	0.23	H-1→L+1 (80%)
5	18394	544	0.003	H-4→LUMO (85%)
	18961	527	0.003	H-1->LUMO (97%)
	20661	484	1.25	HOMO→L+1 (91%)
	26818	373	0.48	H-3→LUMO (31%), H-2→L+1 (53%)
6	18441	542	0.004	H-3→LUMO (86%)
	20675	484	0.64	HOMO→L+1 (93%)
	26134	383	0.74	H-2→LUMO (12%), H-1→L+1 (70%)

Table S 2. Representation of the molecular orbitals HOMO-10 to LUMO+10 of 1

MO		

LUMO+10 (-0.21 eV)		
LUMO+9 (-0.34 eV)		
LUMO+8 (-0.40 eV)		
LUMO+7 (-0.63 eV)		
LUMO+6 (-0.63 eV)		
LUMO+5 (-0.68 eV)		
LUMO+4 (-0.78 eV)		
LUMO+3 (-0.78 eV)		

LUMO+2 (-1.21 eV)		
LUMO+1 (-2.35 eV)		
LUMO (-2.91 eV)		
HOMO (-5.46 eV)		
HOMO-1 (-5.51 eV)		
HOMO-2 (-6.63 eV)		
HOMO-3 (-6.87 eV)		
HOMO-4 (-7.08 eV)		

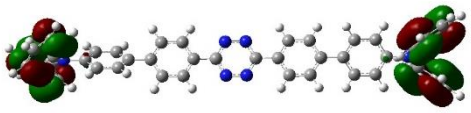
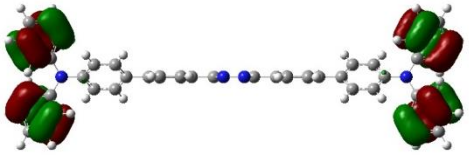
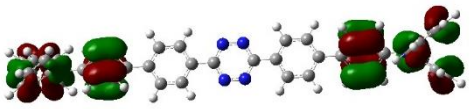
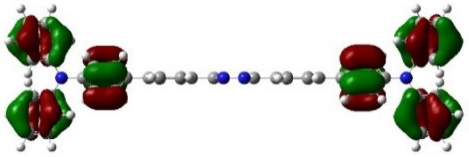
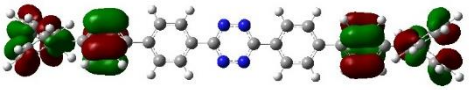
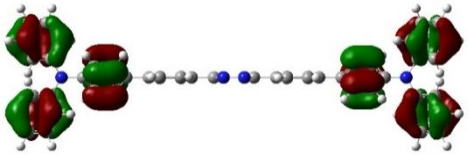
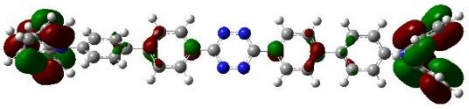
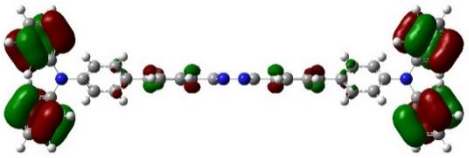
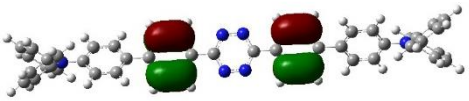
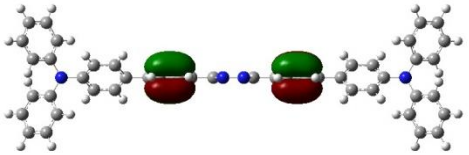
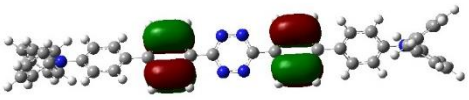
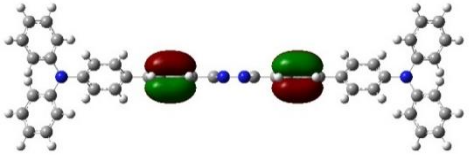
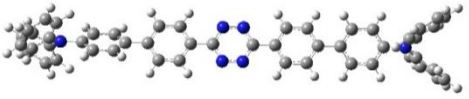
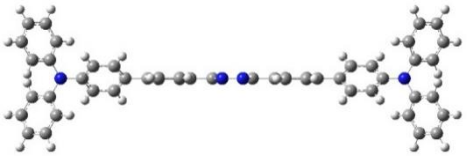
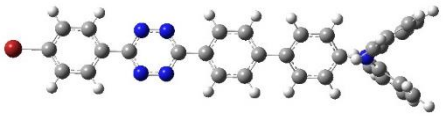
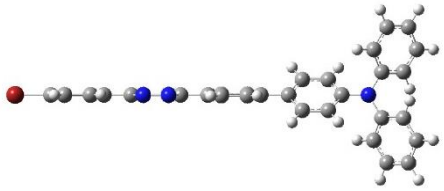
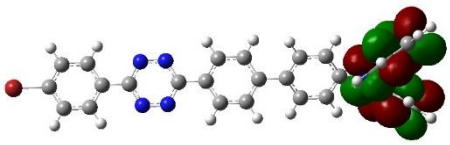
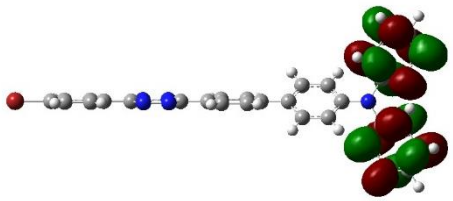
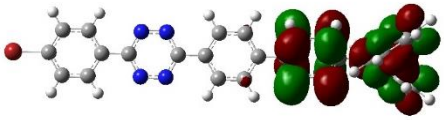
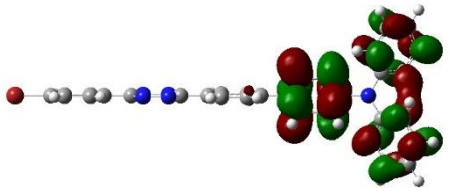
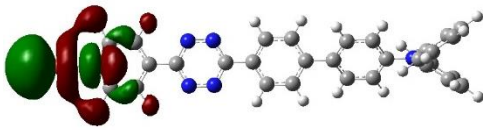
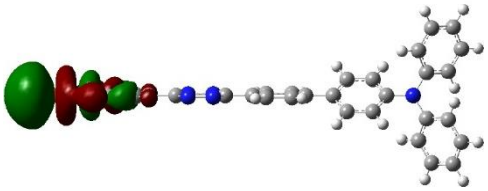
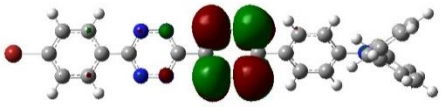
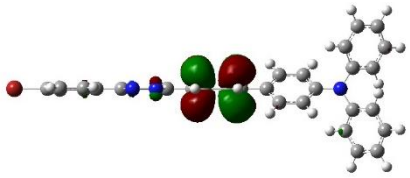
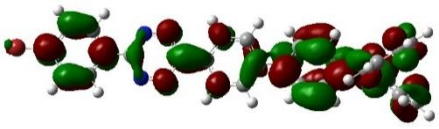
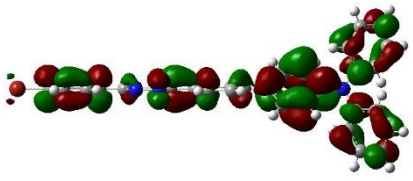
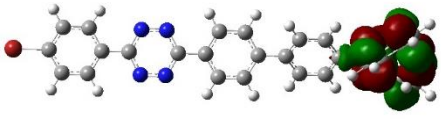
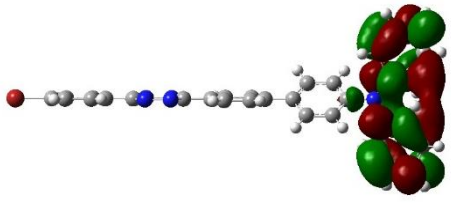
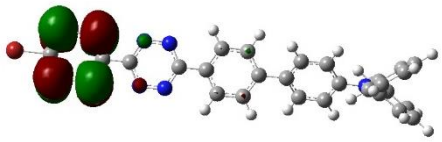
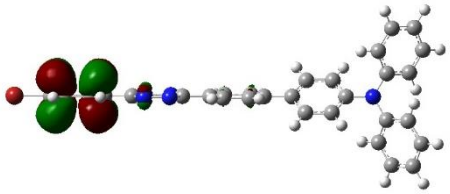
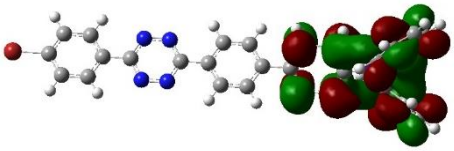
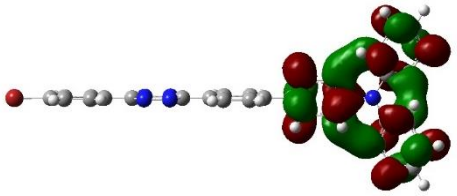
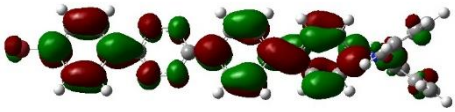
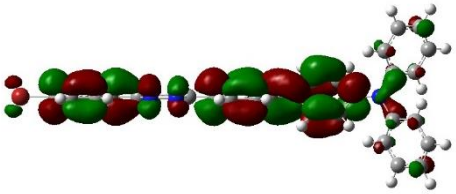
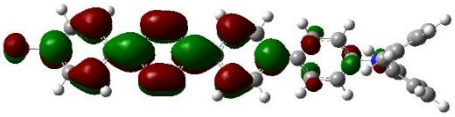
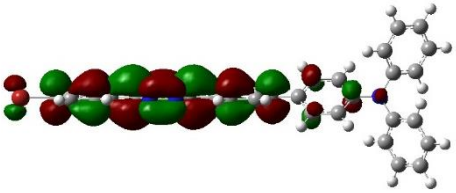
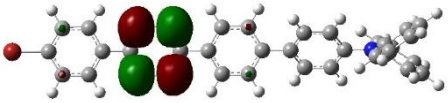
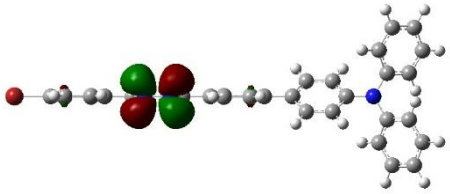
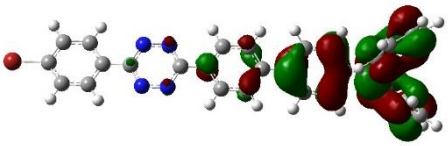
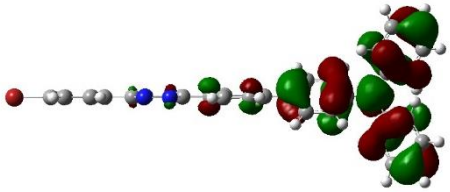
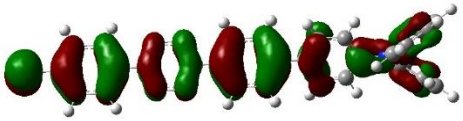
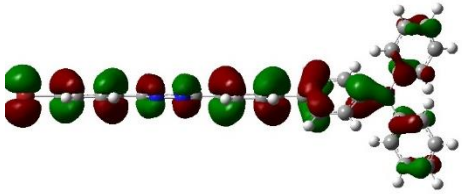
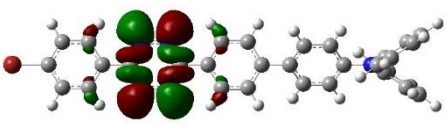
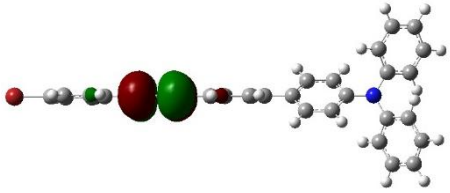
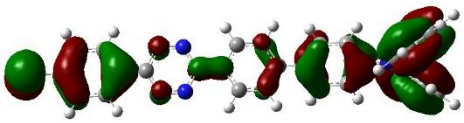
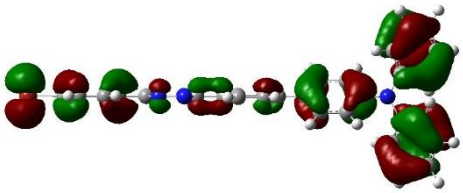
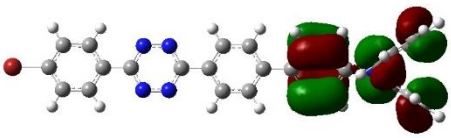
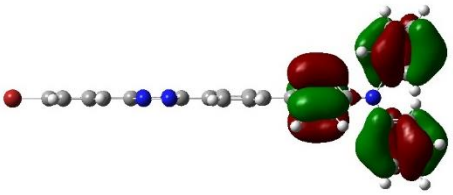
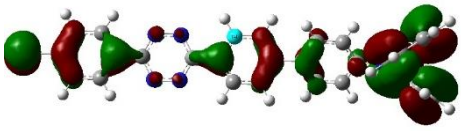
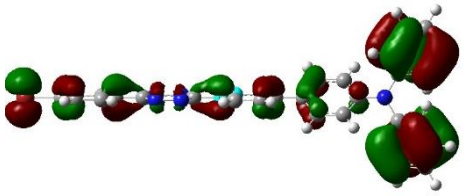
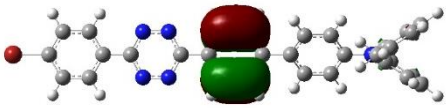
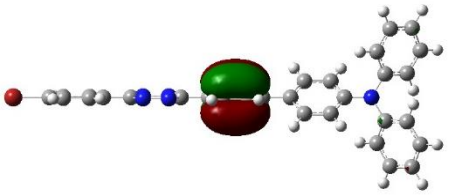
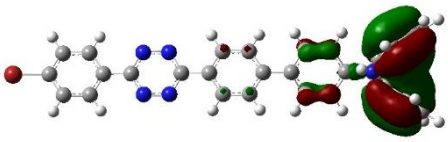
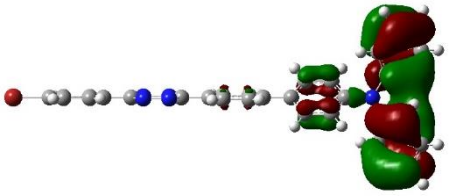
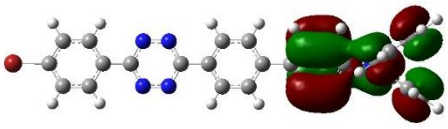
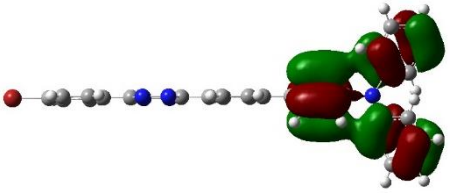
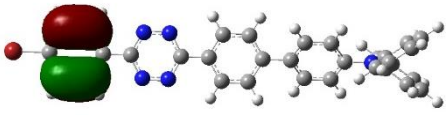
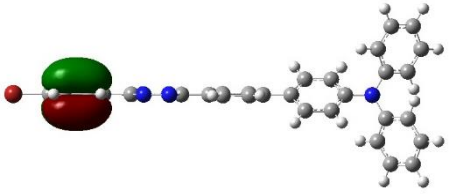
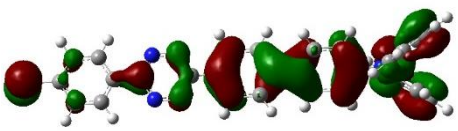
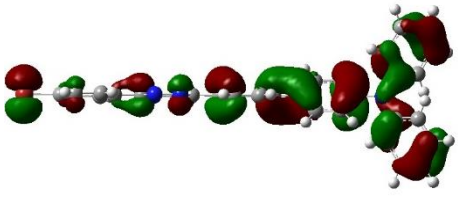
HOMO-5 (-7.29 eV)		
HOMO-6 (-7.31 eV)		
HOMO-7 (-7.31 eV)		
HOMO-8 (-7.33 eV)		
HOMO-9 (-7.51 eV)		
HOMO-10 (-7.52 eV)		
MO		

Table S 3. Representation of the molecular orbitals HOMO-10 to LUMO+10 of 2

MO		
LUMO+10 (-0.16 eV)		
LUMO+9 (-0.20 eV)		
LUMO+8 (-0.40 eV)		
LUMO+7 (-0.47 eV)		
LUMO+6 (-0.49 eV)		
LUMO+5 (-0.69 eV)		

LUMO+4 (-0.73 eV)		
LUMO+3 (-0.84 eV)		
LUMO+2 (-1.23 eV)		
LUMO+1 (-2.52 eV)		
LUMO (-3.10 eV)		
HOMO (-5.55 eV)		
HOMO-1 (-6.80 eV)		
HOMO-2 (-7.07 eV)		

HOMO-3 (-7.29 eV)		
HOMO-4 (-7.38 eV)		
HOMO-5 (-7.42 eV)		
HOMO-6 (-7.62 eV)		
HOMO-7 (-7.66 eV)		
HOMO-8 (-7.67 eV)		
HOMO-9 (-7.90 eV)		
HOMO-10 (-8.04 eV)		

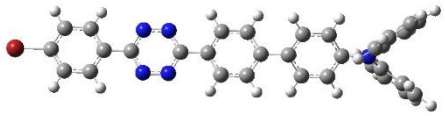
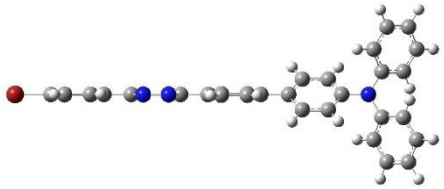
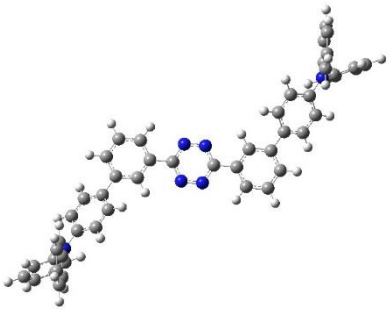
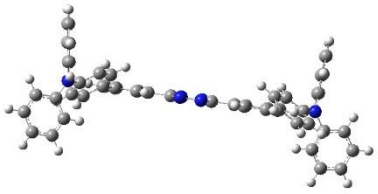
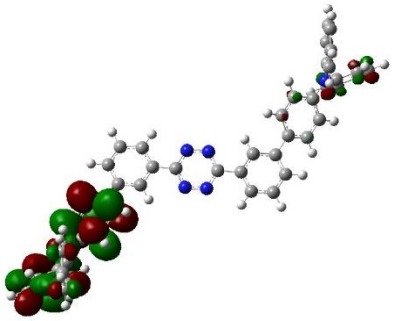
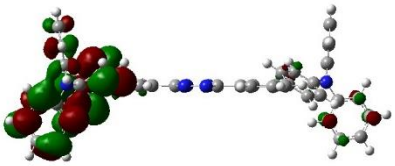
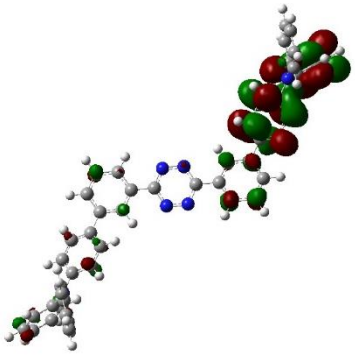
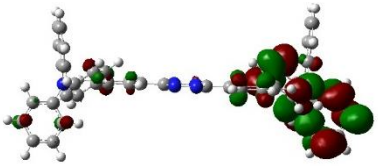
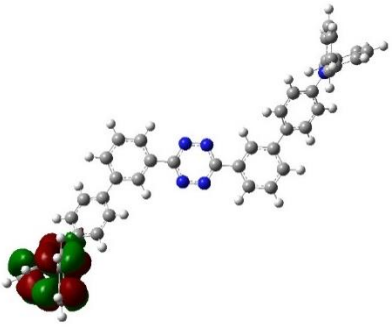
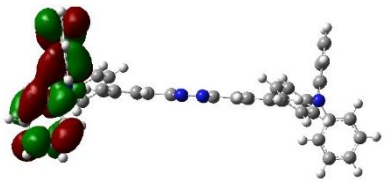
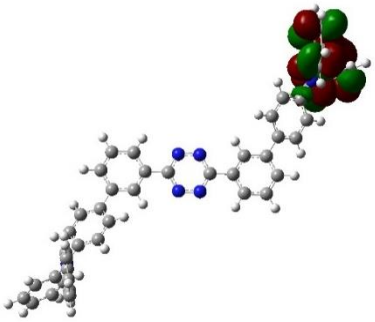
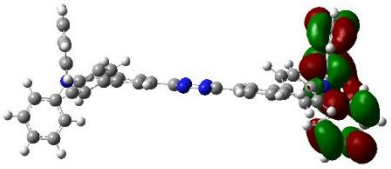
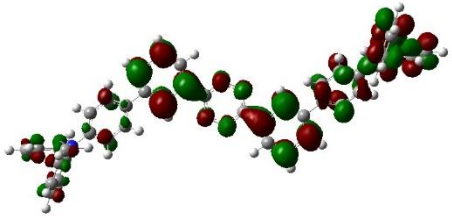
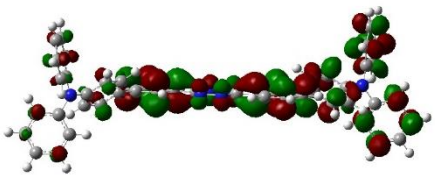
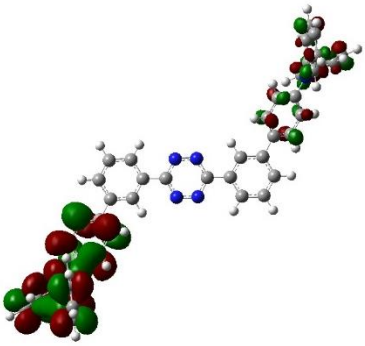
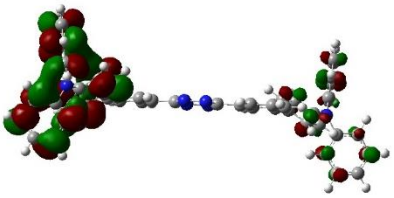
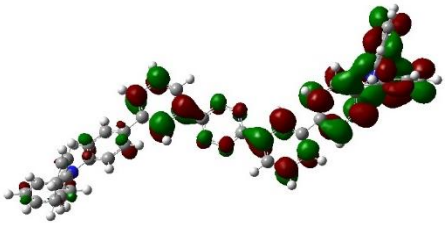
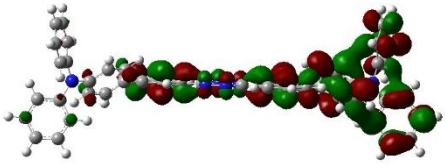
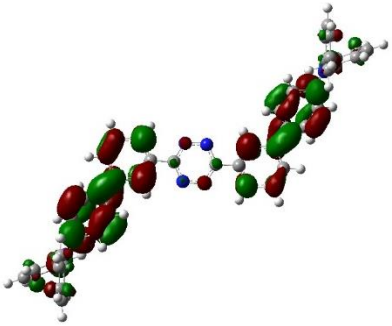
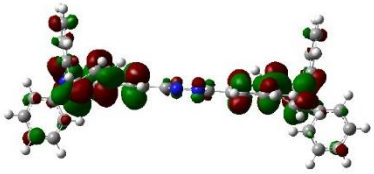
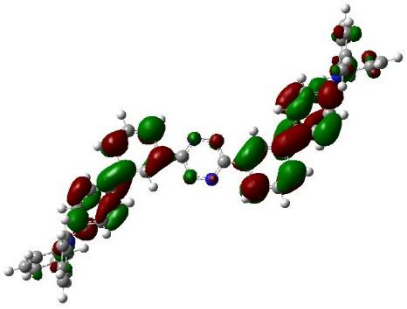
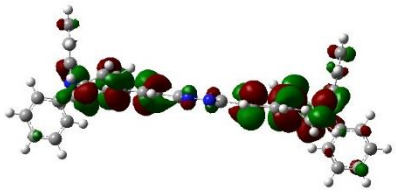
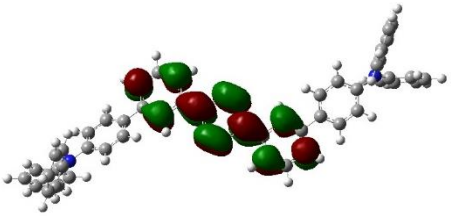
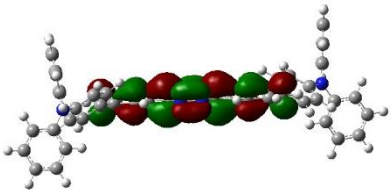
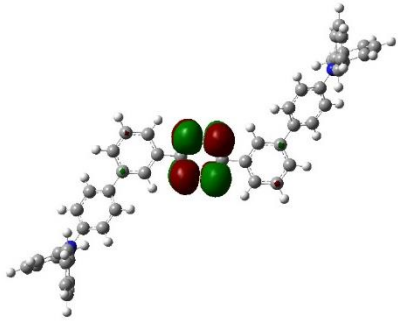
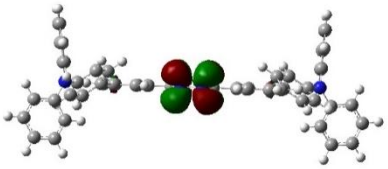
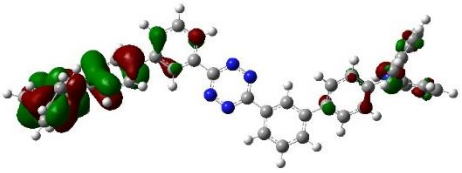
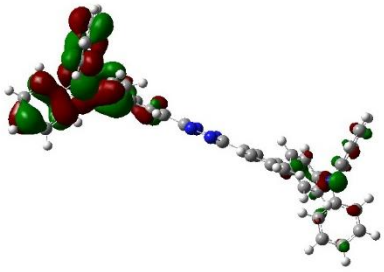
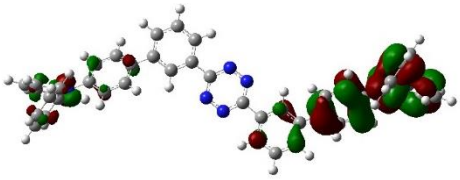
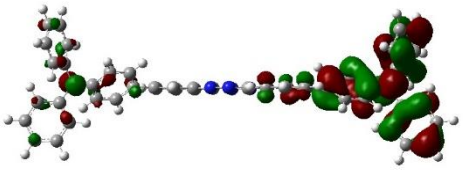
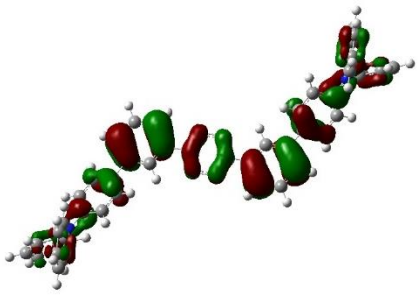
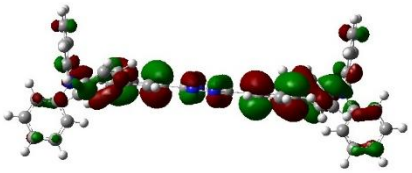
MO		

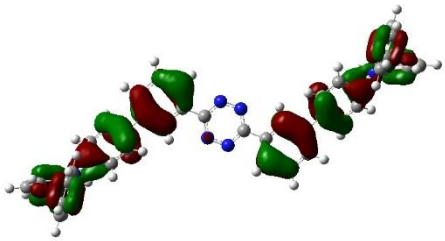
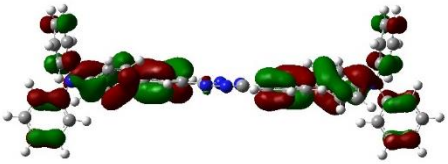
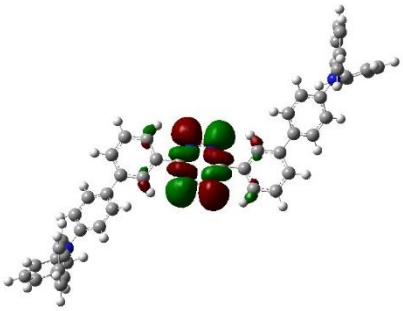
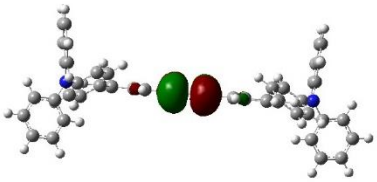
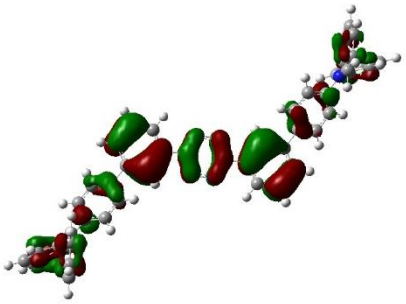
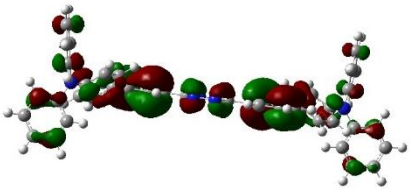
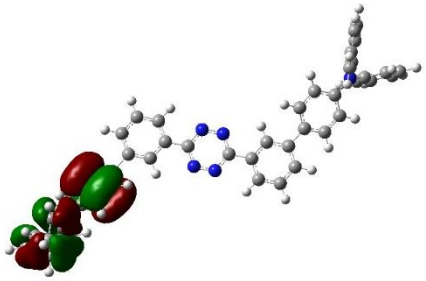
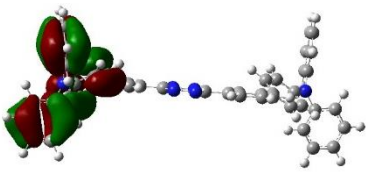
Table S 4. Representation of the molecular orbitals HOMO-10 to LUMO+10 of 3

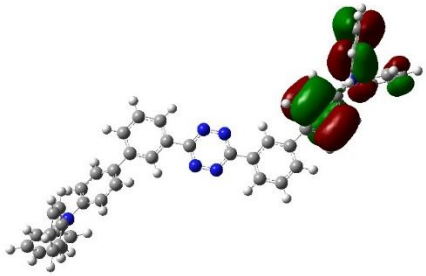
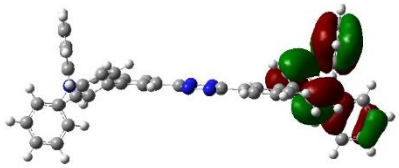
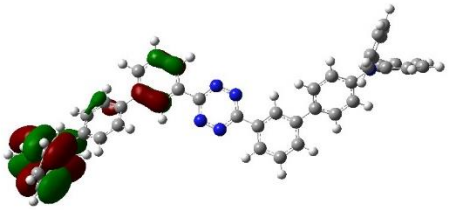
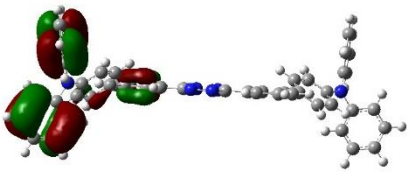
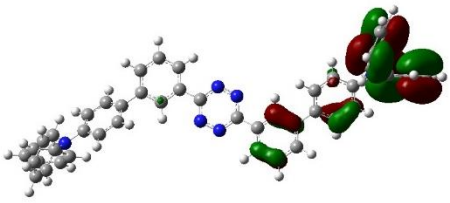
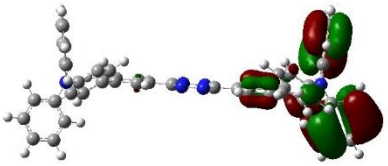
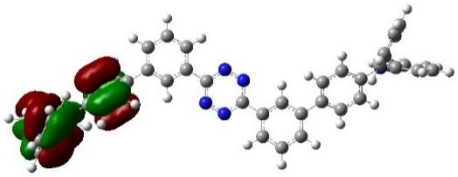
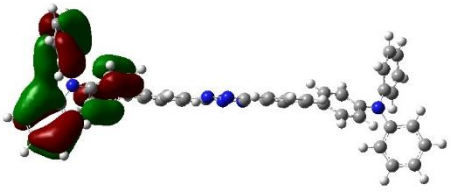
MO		
LUMO+10 (-0.10 eV)		
LUMO+9 (-0.11 eV)		

LUMO+8 (-0.59 eV)		
LUMO+7 (-0.60 eV)		
LUMO+6 (-0.67 eV)		
LUMO+5 (-0.73 eV)		

LUMO+4 (-0.75 eV)		
LUMO+3 (-1.01 eV)		
LUMO+2 (-1.12 eV)		
LUMO+1 (-2.33 eV)		

LUMO (-2.99 eV)		
HOMO (-5.45 eV)		
HOMO-1 (-5.45 eV)		
HOMO-2 (-6.81 eV)		

HOMO-3 (-6.95 eV)		
HOMO-4 (-6.96 eV)		
HOMO-5 (-7.11 eV)		
HOMO-6 (-7.26 eV)		

HOMO-7 (-7.26 eV)		
HOMO-8 (-7.28 eV)		
HOMO-9 (-7.29 eV)		
HOMO-10 (-7.54 eV)		

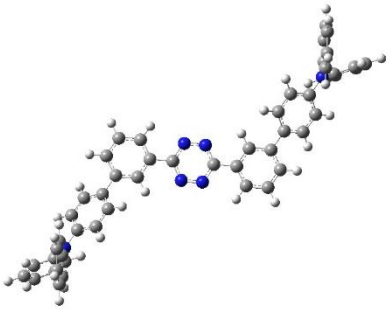
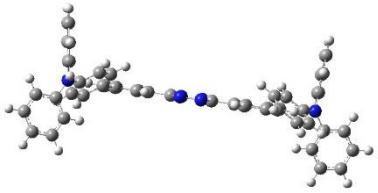
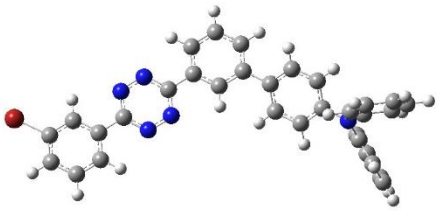
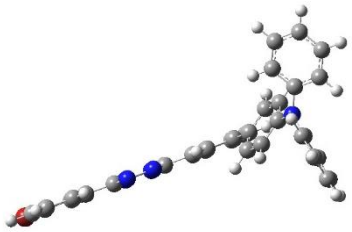
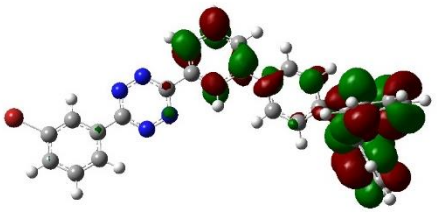
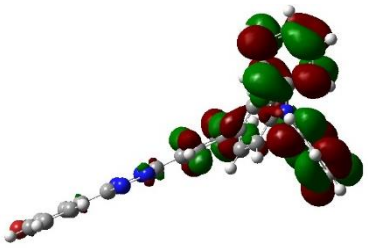
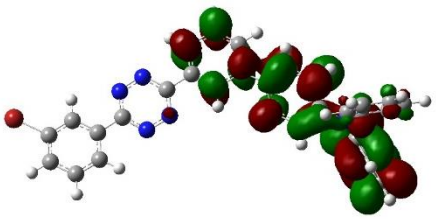
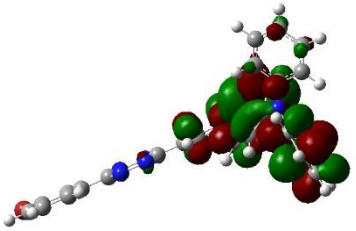
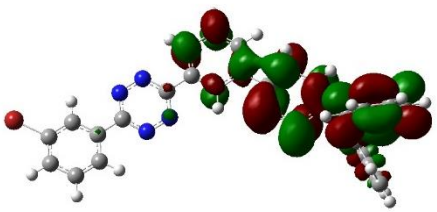
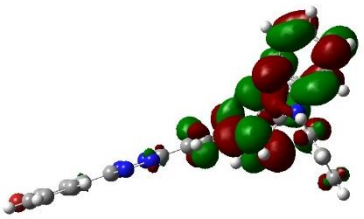
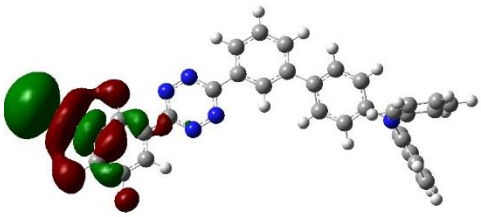
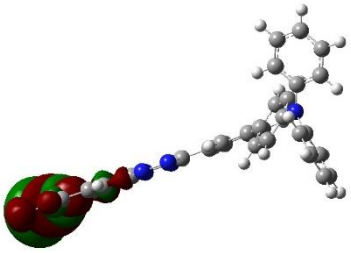
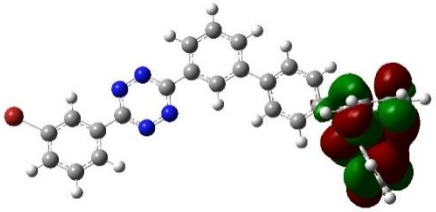
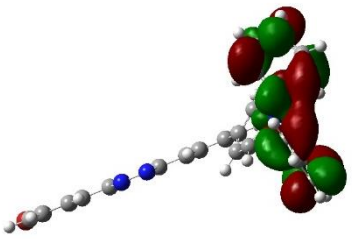
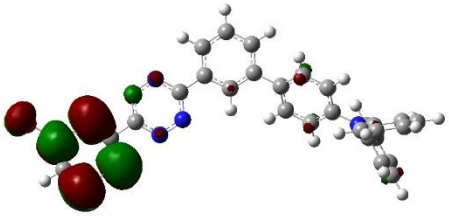
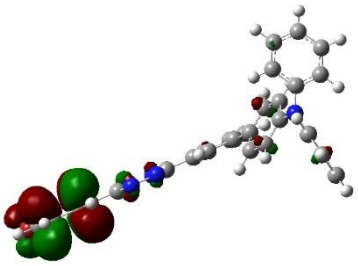
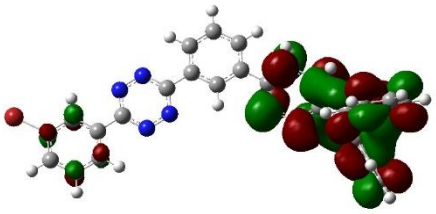
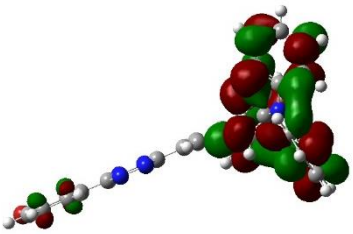
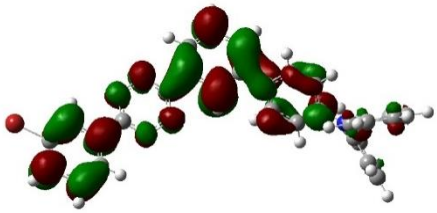
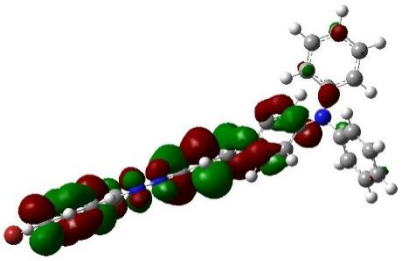
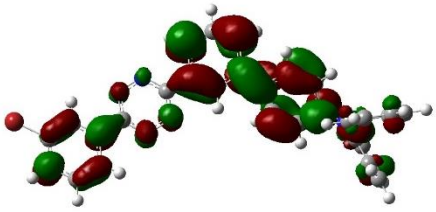
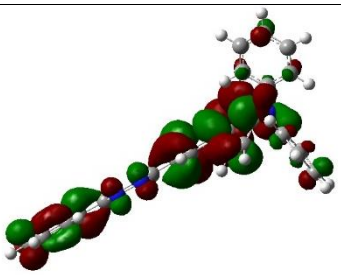
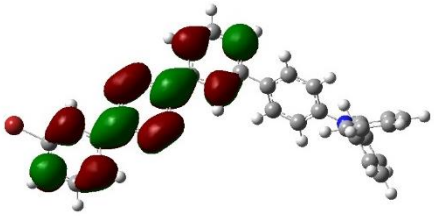
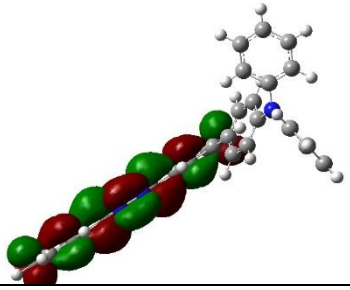
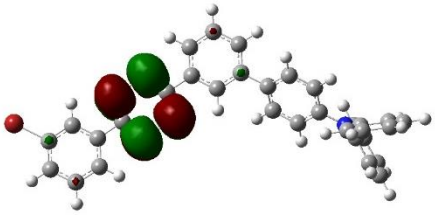
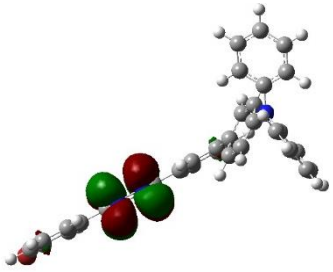
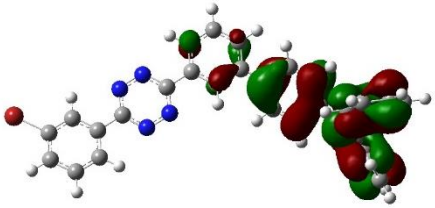
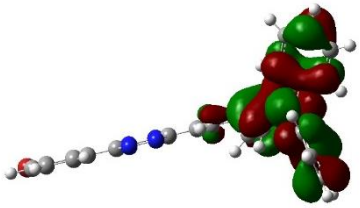
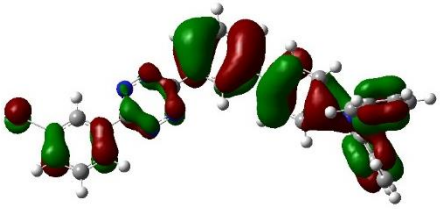
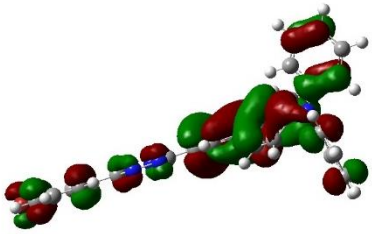
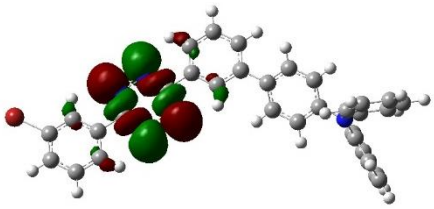
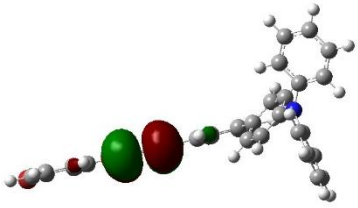
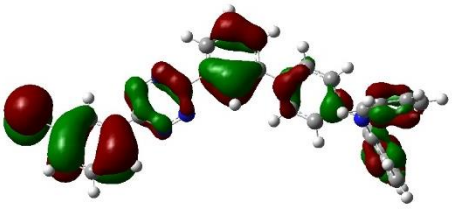
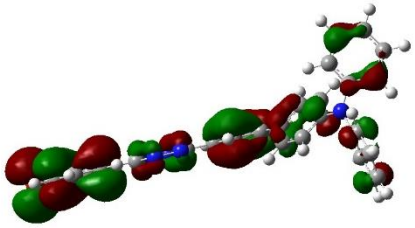
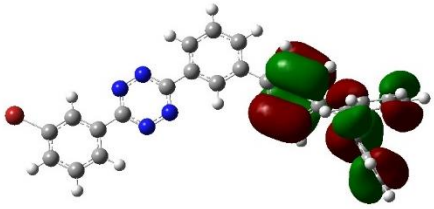
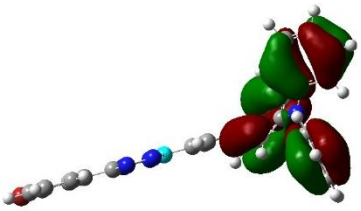
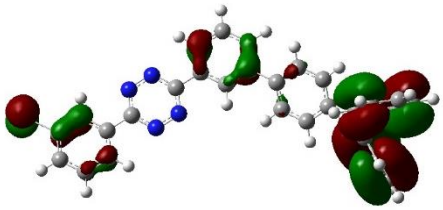
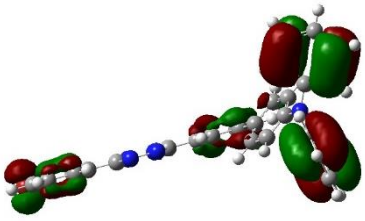
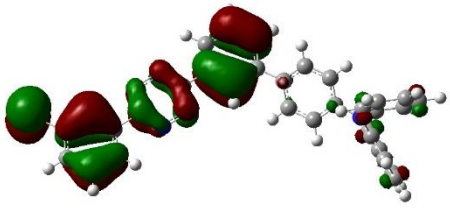
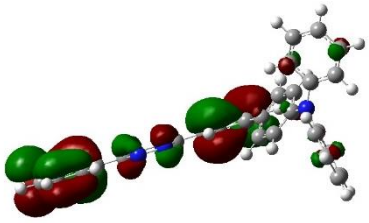
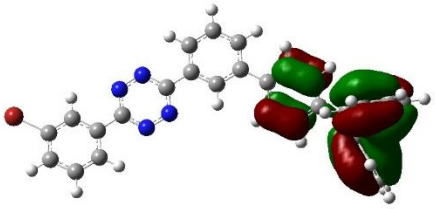
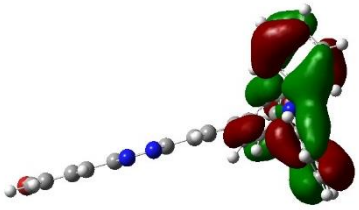
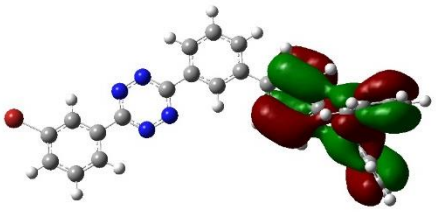
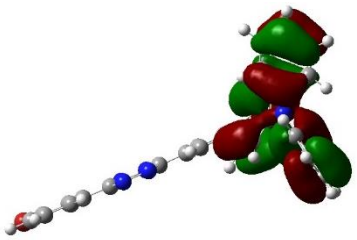
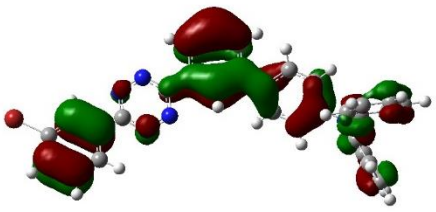
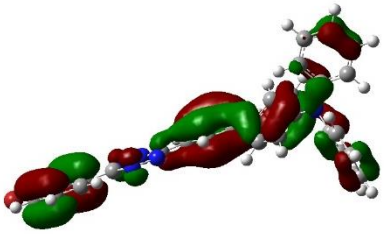
MO		

Table S 5. Representation of the molecular orbitals HOMO-10 to LUMO+10 of 4

MO		
LUMO+10 (-0.08 eV)		
LUMO+9 (-0.15 eV)		
LUMO+8 (-0.16 eV)		

LUMO+7 (-0.39 eV)		
LUMO+6 (-0.63 eV)		
LUMO+5 (-0.75 eV)		
LUMO+4 (-0.78 eV)		
LUMO+3 (-0.90 eV)		
LUMO+2 (-1.16 eV)		

LUMO+1 (-2.54 eV)		
LUMO (-3.18 eV)		
HOMO (-5.50 eV)		
HOMO-1 (-6.97 eV)		
HOMO-2 (-7.15 eV)		
HOMO-3 (-7.18 eV)		

HOMO-4 (-7.31 eV)		
HOMO-5 (-7.33 eV)		
HOMO-6 (-7.43 eV)		
HOMO-7 (-7.59 eV)		
HOMO-8 (-7.61 eV)		
HOMO-9 (-7.94 eV)		

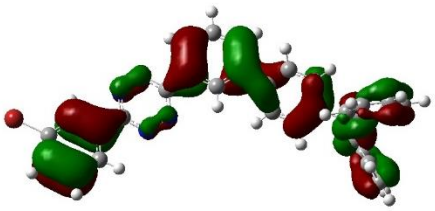
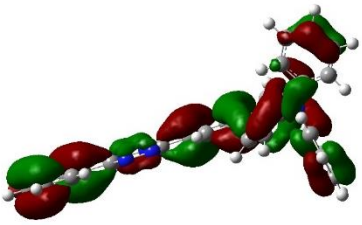
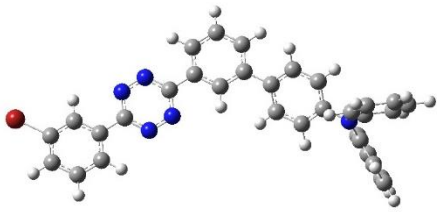
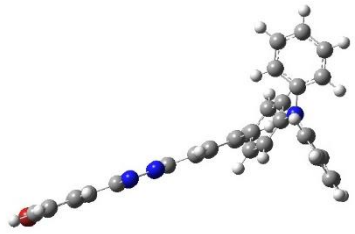
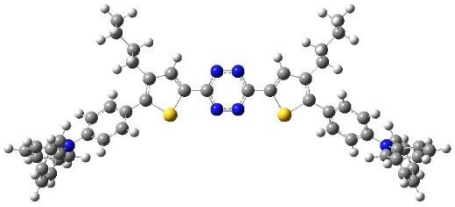
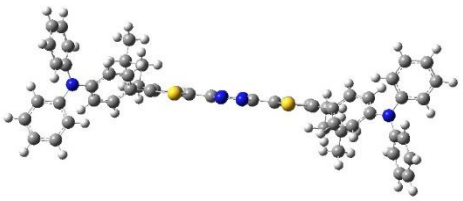
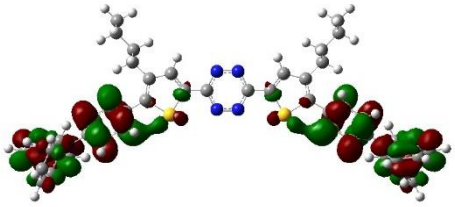
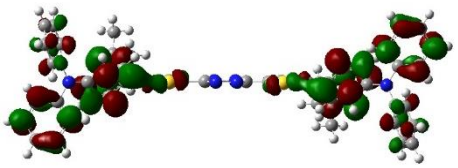
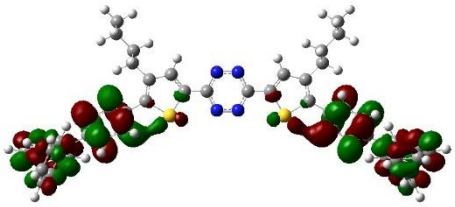
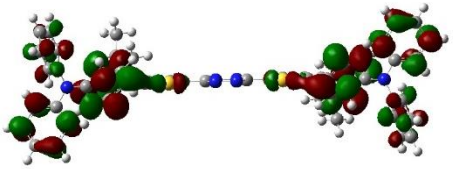
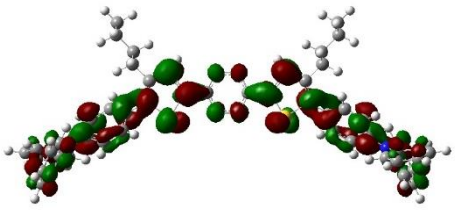
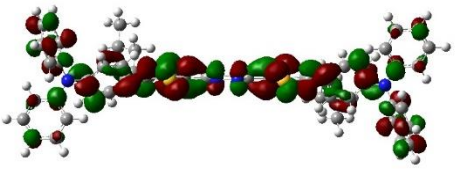
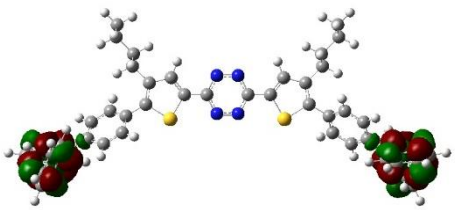
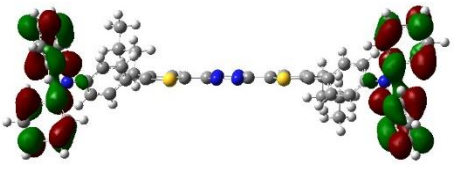
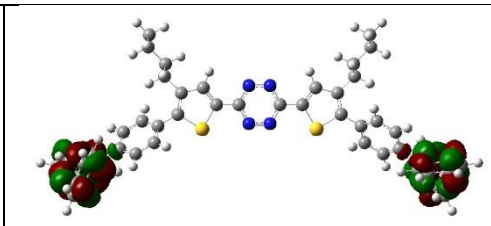
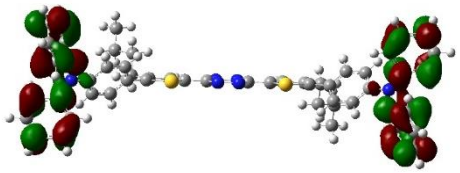
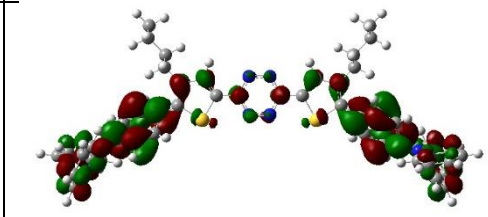
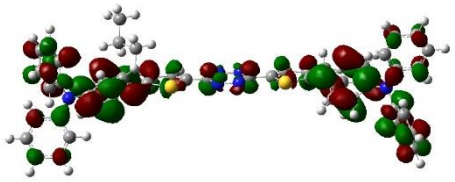
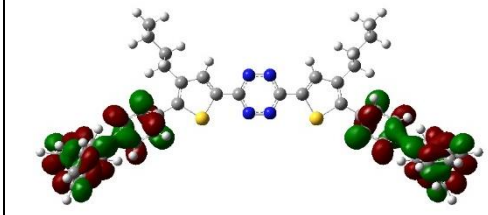
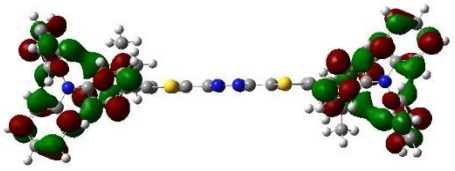
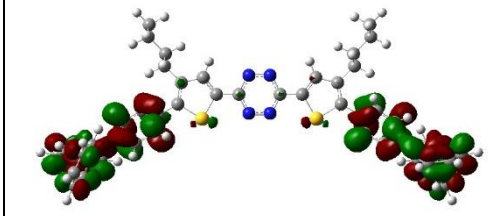
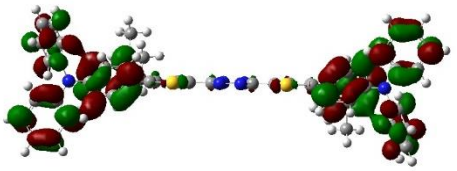
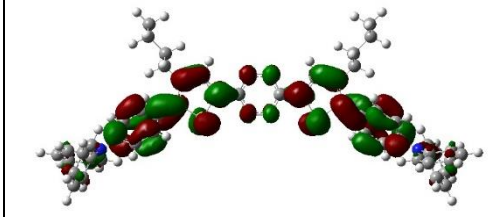
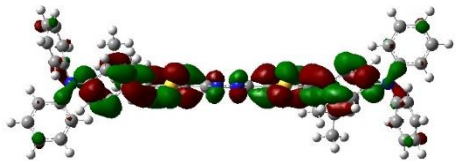
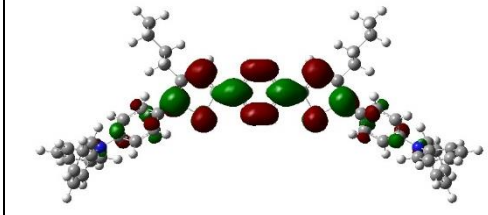
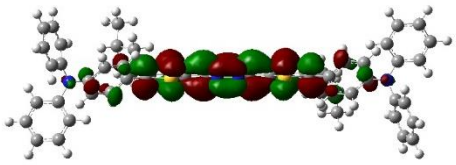
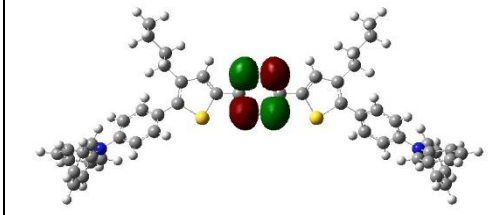
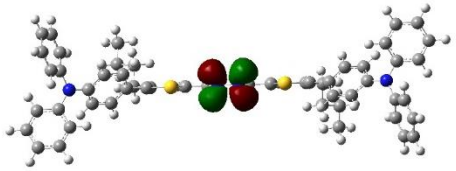
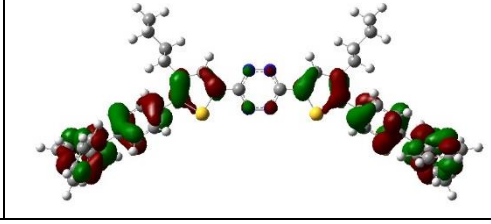
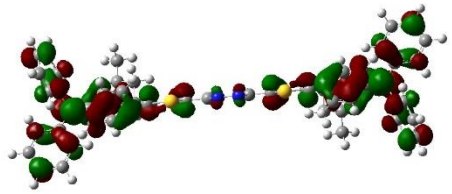
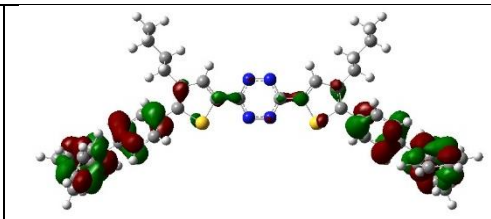
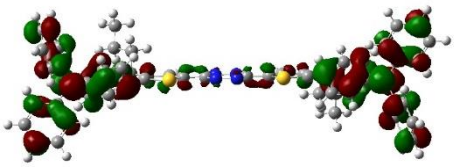
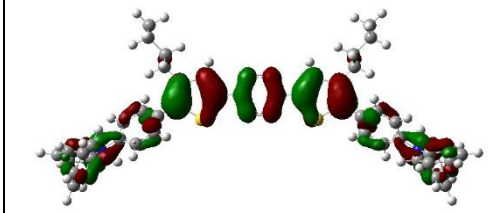
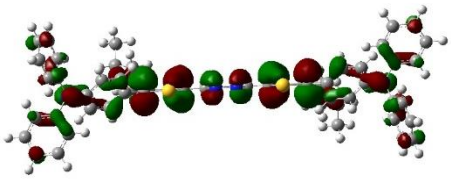
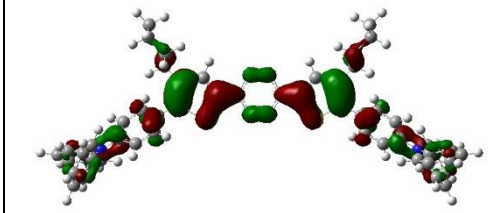
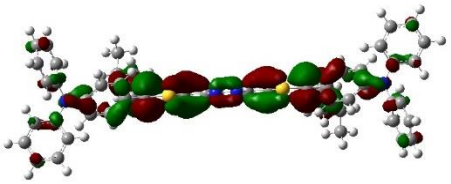
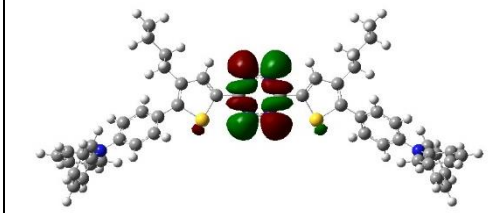
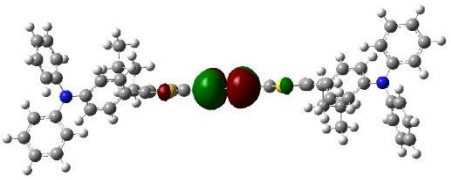
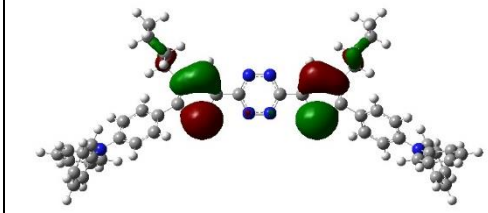
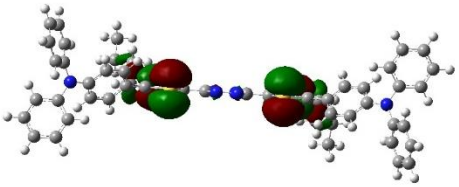
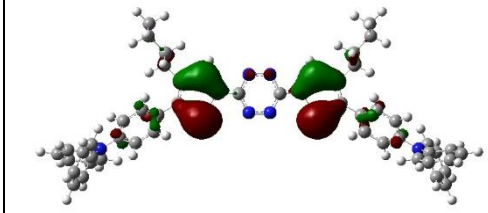
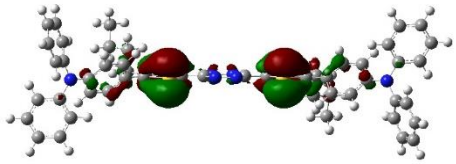
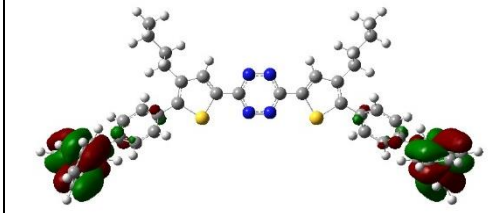
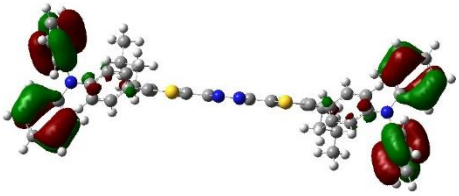
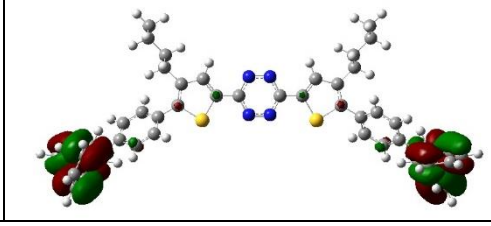
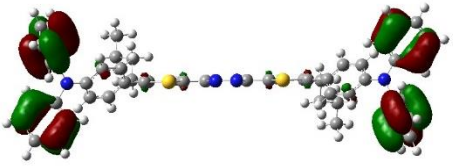
HOMO-10 (-8.13 eV)		
MO		

Table S 6. Representation of the molecular orbitals HOMO-10 to LUMO+10 of 5

MO		
LUMO+10 (-0.20 eV)		
LUMO+9 (-0.20 eV)		
LUMO+8 (-0.42 eV)		
LUMO+7 (-0.65 eV)		

LUMO+6 (-0.65 eV)		
LUMO+5 (-0.80 eV)		
LUMO+4 (-0.81 eV)		
LUMO+3 (-0.82 eV)		
LUMO+2 (-1.24 eV)		
LUMO+1 (-2.39 eV)		
LUMO (-2.76 eV)		
HOMO (-5.43 eV)		

HOMO-1 (-5.53 eV)		
HOMO-2 (-6.21 eV)		
HOMO-3 (-6.80 eV)		
HOMO-4 (-6.84 eV)		
HOMO-5 (-7.11 eV)		
HOMO-6 (-7.11 eV)		
HOMO-7 (-7.30 eV)		
HOMO-8 (-7.33 eV)		

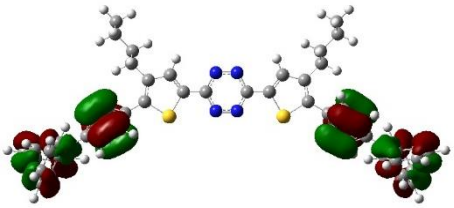
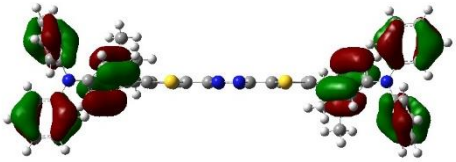
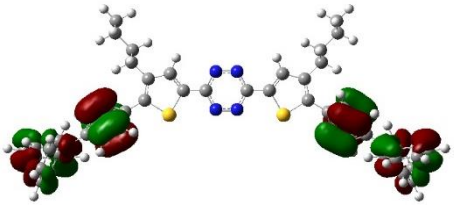
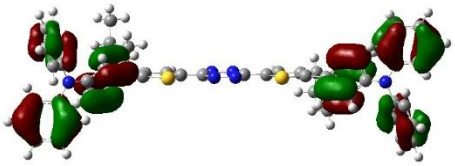
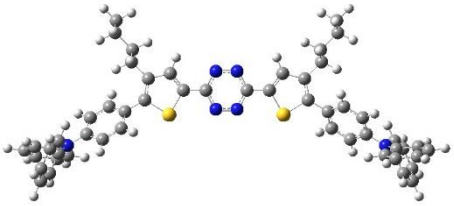
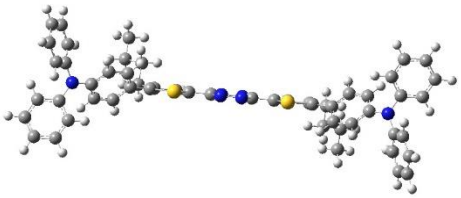
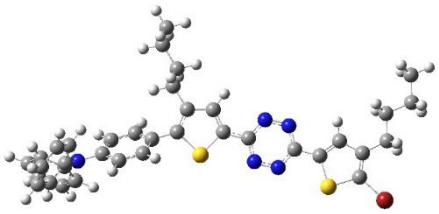
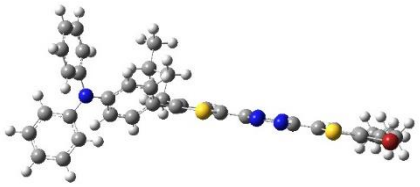
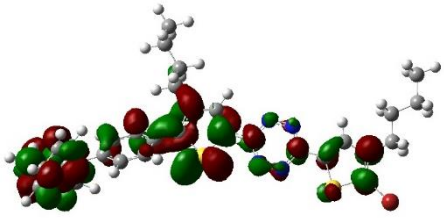
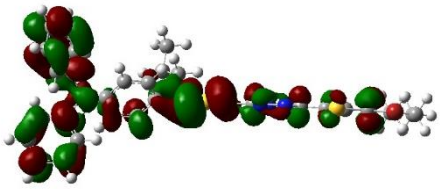
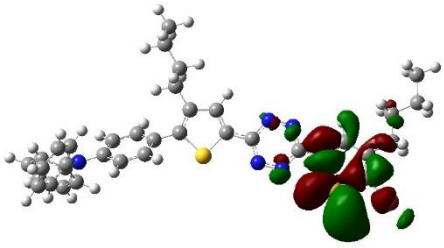
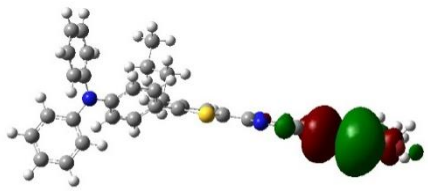
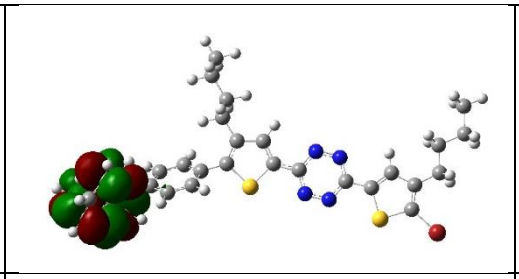
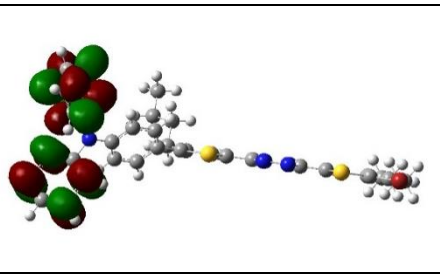
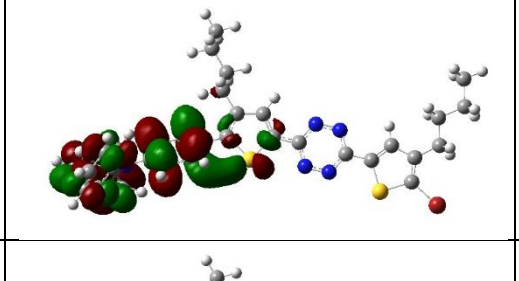
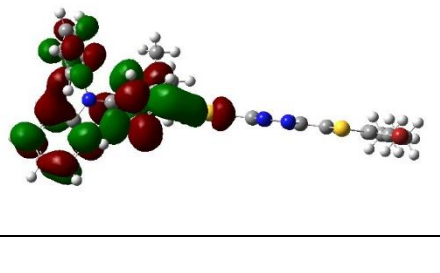
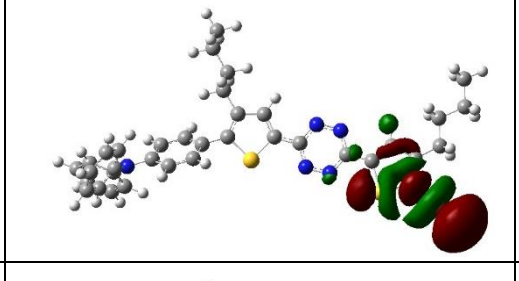
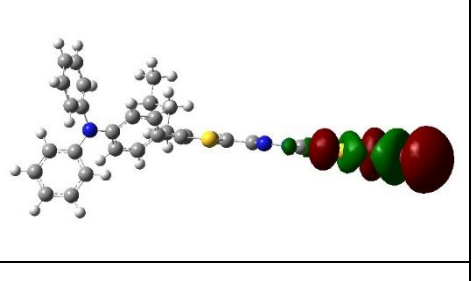
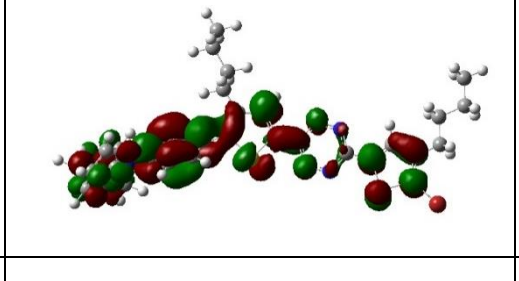
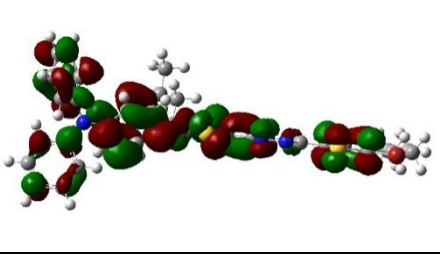
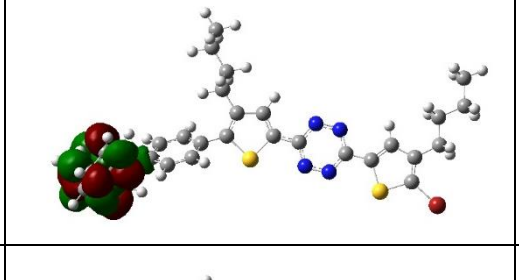
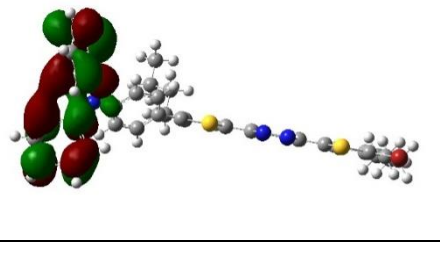
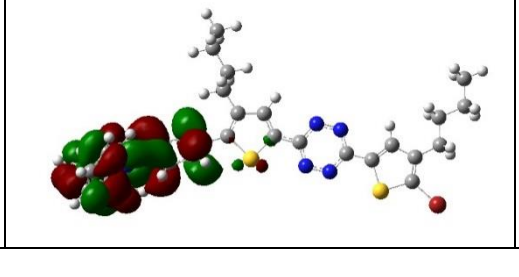
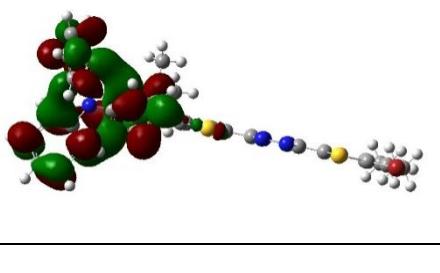
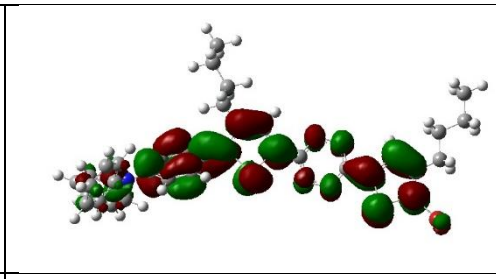
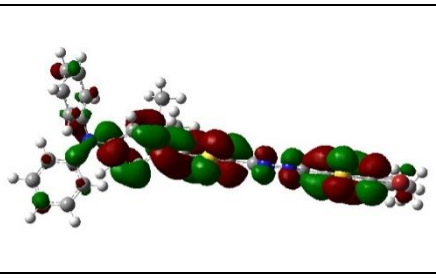
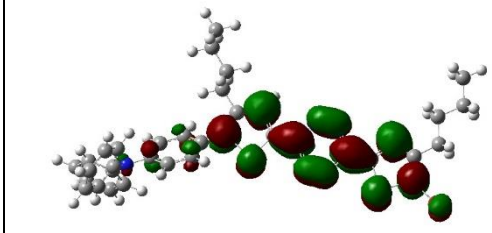
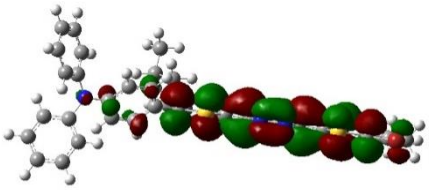
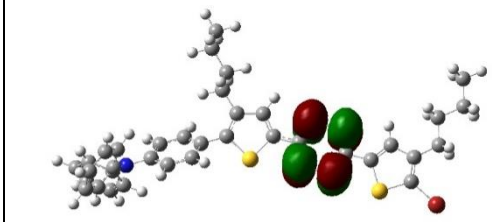
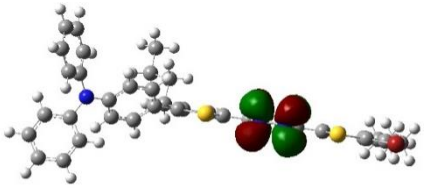
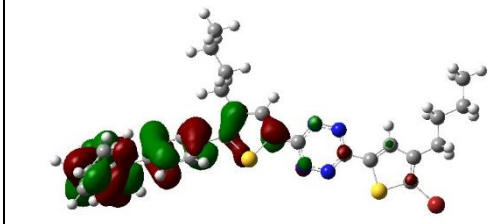
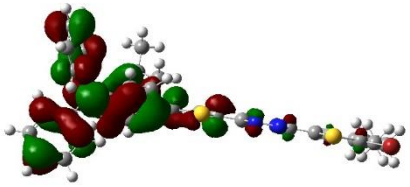
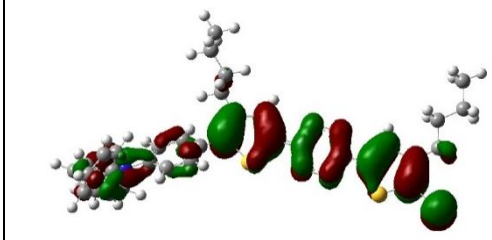
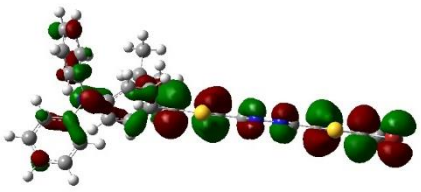
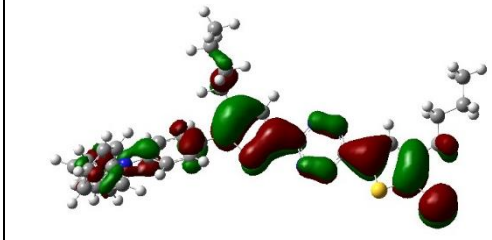
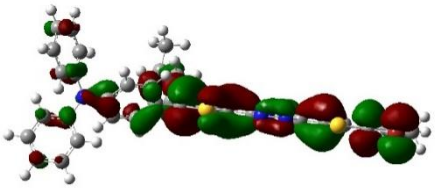
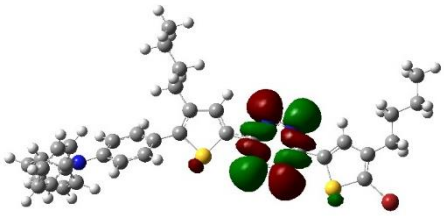
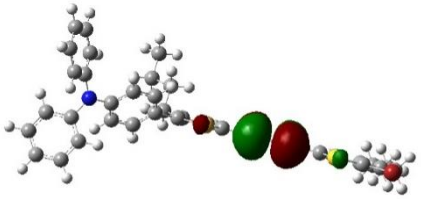
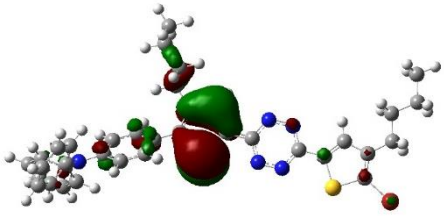
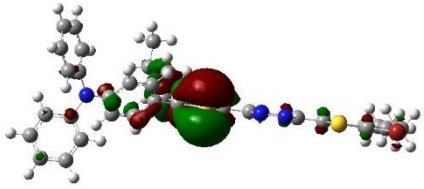
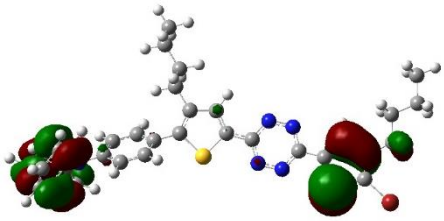
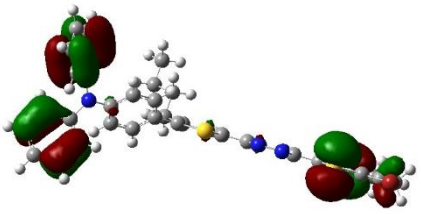
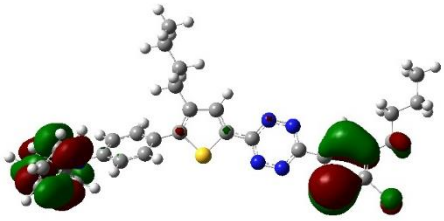
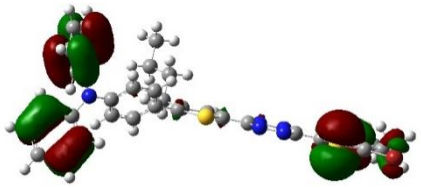
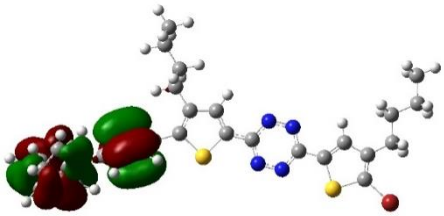
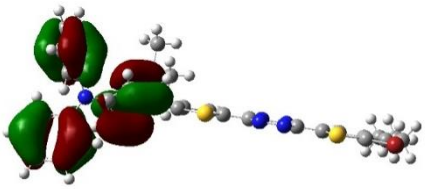
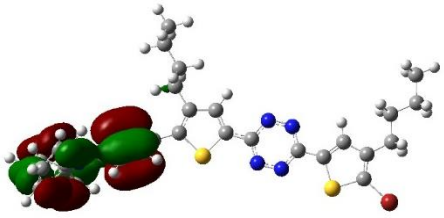
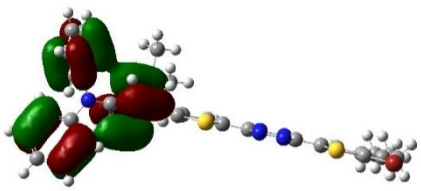
HOMO-9 (-7.34 eV)		
HOMO-10 (-7.34 eV)		
MO		

Table S 7. Representation of the molecular orbitals HOMO-10 to LUMO+10 of 6

MO		
LUMO+10 (0.03 eV)		
LUMO+9 (0.00 eV)		

LUMO+8 (-0.17 eV)		
LUMO+7 (-0.27 eV)		
LUMO+6 (-0.52 eV)		
LUMO+5 (-0.70 eV)		
LUMO+4 (-0.70 eV)		
LUMO+3 (-0.86 eV)		

LUMO+2 (-1.28 eV)		
LUMO+1 (-2.56 eV)		
LUMO (-2.94 eV)		
HOMO (-5.54 eV)		
HOMO-1 (-6.31 eV)		
HOMO-2 (-6.97 eV)		

HOMO-3 (-7.03 eV)		
HOMO-4 (-7.22 eV)		
HOMO-5 (-7.37 eV)		
HOMO-6 (-7.39 eV)		
HOMO-7 (-7.50 eV)		
HOMO-8 (-7.67 eV)		

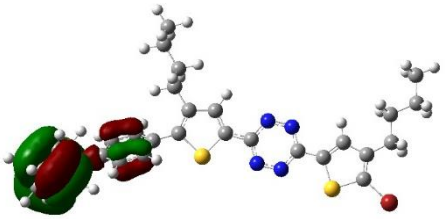
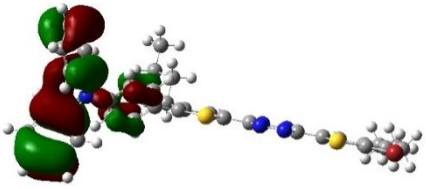
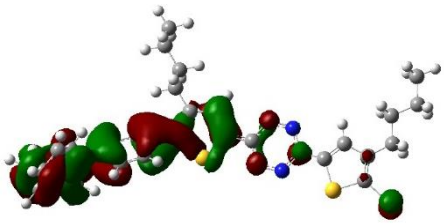
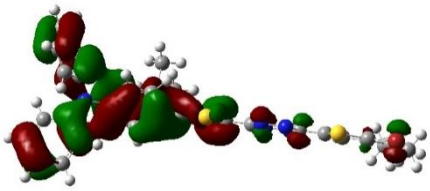
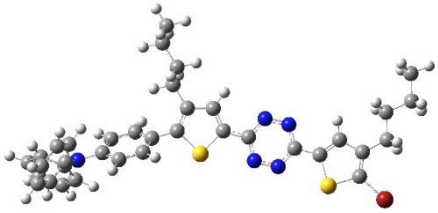
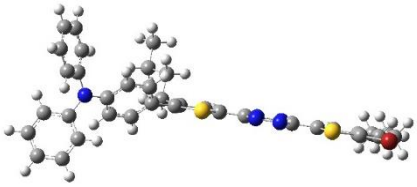
HOMO-9 (-7.68 eV)		
HOMO-10 (-7.85 eV)		
MO		

Table S 8. 12 first calculated transitions of 1

λ (nm)	λ (eV)	Oscillator strength	Major contributing molecular orbitals	Transition type
572	2.17	0.0031	**H-3->LUMO (80%)**	n → π* Tz
572	2.17	0.0003	**HOMO->LUMO (97%)**	CT TPA→Tz
554	2.24	0.0002	**H-1->LUMO (93%)**	CT TPA→Tz
462	2.68[a]	1.1820	**HOMO->L+1 (94%)**	CT TPA→Tz-Ph
442	2.81[a]	0.0000	**H-1->L+1 (96%)**	CT TPA→Tz-Ph
401	3.09	0.0033	**H-2->LUMO (90%)**	π→π* Tz-Ph→Tz
390	3.18	0.0000	**H-3->L+1 (94%)**	n → π* Tz-Ph
350	3.54	0.0000	**H-4->LUMO (87%)**	π→π* TPA-Ph→Tz
338	3.67	1.4632	**H-2->L+1 (59%),** H-1->L+2 (22%)	π→π* Tz-Ph→Tz-Ph
331	3.75	0.0000	H-1->L+5 (11%), **HOMO->L+2 (81%)**	π→π* TPA→TPA-Ph
329	3.77	0.1944	**H-9->LUMO (71%),** H-1->L+2 (20%)	π→π* Ph→Tz
326	3.80	0.0000	**H-10->LUMO (97%)**	π→π* Ph→Tz

[a] These values are used for the calculations shown in Figure 7.

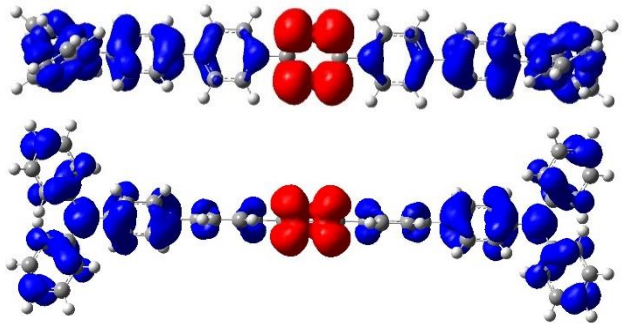


Figure S 10. Calculated electron density changes accompanying the second electronic excitation of 1. The blue and red lobes signify decreases and increases respectively in electron density accompanying the electronic transition. Their areas indicate the magnitude of the electron density change (isodensity=0.0004).

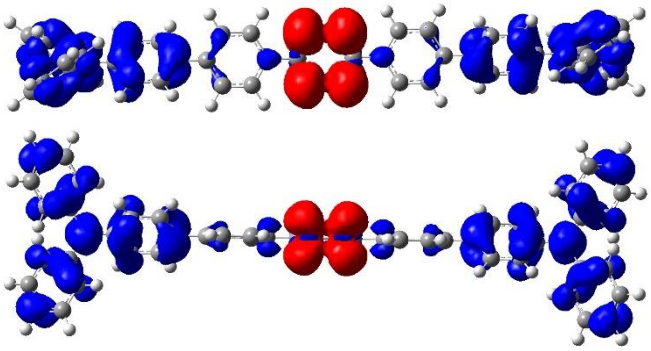


Figure S 11. Calculated electron density changes accompanying the third electronic excitation of 1. The blue and red lobes signify decreases and increases respectively in electron density accompanying the electronic transition. Their areas indicate the magnitude of the electron density change (isodensity=0.0004).

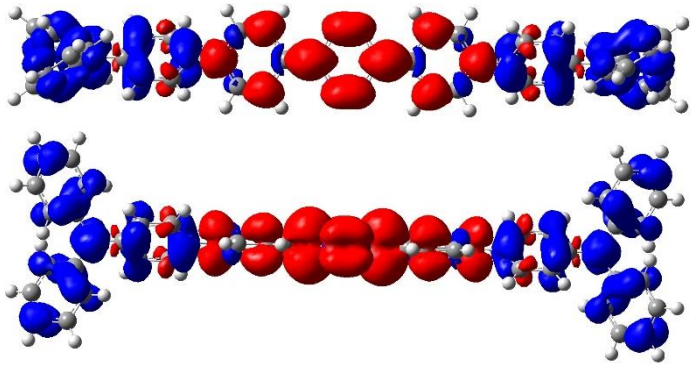


Figure S 12. Calculated electron density changes accompanying the fourth electronic excitation of 1. The blue and red lobes signify decreases and increases respectively in electron density accompanying the electronic transition. Their areas indicate the magnitude of the electron density change (isodensity=0.0004).

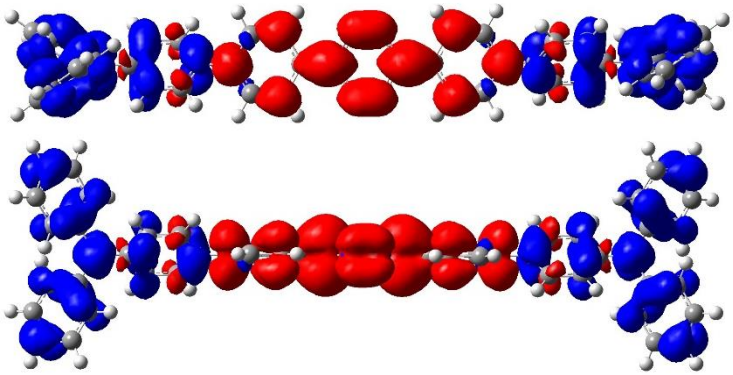


Figure S 13. Calculated electron density changes accompanying the fifth electronic excitation of 1. The blue and red lobes signify decreases and increases respectively in electron density accompanying the electronic transition. Their areas indicate the magnitude of the electron density change (isodensity=0.0004).

Table S 9. 12 first calculated transitions of 2

λ (nm)	λ (eV)	Oscillator strength	Major contributing molecular orbitals	Transition type
600	2.07	0.0002	**HOMO->LUMO (97%)**	CT TPA→Tz
570	2.18	0.0034	**H-2->LUMO (84%)**	n → π* Tz
472	2.63	0.5070	**HOMO->L+1 (95%)**	CT TPA→Tz-Ph
410	3.02	0.0034	**H-1->LUMO (90%)**	π→π* Tz-Ph→Tz
392	3.16	0.0003	**H-2->L+1 (95%)**	n → π* Tz-Ph
352	3.52	0.0001	H-5->LUMO (34**%),** **H-3->LUMO (58%)**	CT TPA-Ph→Tz
340	3.65	1.1409	**H-1->L+1 (55%),** HOMO->L+2 (22%)	π→π* Tz-Ph→Tz-Ph
334	3.71	0.2697	H-7->LUMO (33%), **H-6->LUMO (40%),** HOMO->L+2 (21%)	π→π* Ph→Tz
327	3.79	0.0128	**HOMO->L+3 (94%)**	π→π* TPA→TPA
325	3.81	0.1232	H-1->L+1 (30**%),** **HOMO->L+2 (42%)**	π→π* TPA→Ph-Ph-Br
317	3.91	0.0000	**H-4->LUMO (94%)**	CT TPA→Tz
314	3.95	0.0001	**H-5->LUMO (60%),** H-3->LUMO (38%)	CT TPA→Tz

There is one calculated CT transition at lower energy (CT1 600 nm [2.07ev]) than the main one (CT2 472 nm [2.63 eV]) but with lower oscillator strength. By scaling the value of the CT1 band using the difference in energy between the calculated and experimental main CT2 band (i.e. the difference between calculated CT2 (472nm, 2.63 eV) and experimental CT2 (401 nm, 3.09 eV): 0.46 eV), the CT1 band can be estimated to be found at 2.07+0.46= 2.53 eV (490 nm) and the difference with λ_{TPA} is 2*1.48-2.53= 0.43 eV.

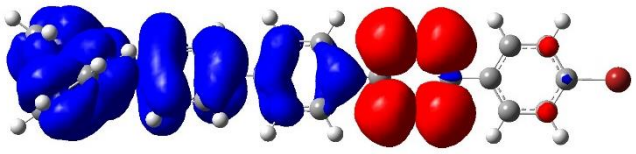


Figure S 14. Calculated electron density changes accompanying the first electronic excitation of 2. The blue and red lobes signify decreases and increases respectively in electron density accompanying the electronic transition. Their areas indicate the magnitude of the electron density change (isodensity=0.0004).

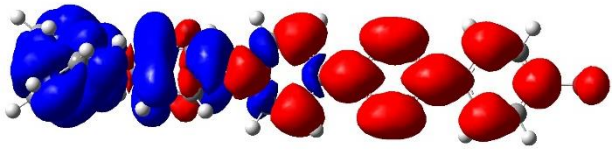


Figure S 15. Calculated electron density changes accompanying the third electronic excitation of 2. The blue and red lobes signify decreases and increases respectively in electron density accompanying the electronic transition. Their areas indicate the magnitude of the electron density change (isodensity=0.0004).

Table S 10. 12 first calculated transitions of 5

λ (nm)	λ (eV)	Oscillator strength	Major contributing molecular orbitals	Transition type
567	2.19	0.0004	**HOMO->LUMO (91%)**	CT TPA-Th→Tz
544	2.28	0.0033	**H-4->LUMO (85%)**	n → π* Tz
527	2.35	0.0033	**H-1->LUMO (97%)**	CT TPA→Tz
484	2.56[a]	1.2500	**HOMO->L+1 (91%)**	CT TPA-Th→Tz-Th
450	2.76[a]	0.0568	**H-1->L+1 (96%)**	CT TPA→ Tz-Th
433	2.86	0.0037	**H-2->LUMO (88%)**	π→π* Tz-Th→Tz
393	3.15	0.0000	**H-4->L+1 (95%)**	n → π* Tz-Th
375	3.31	0.1703	**H-3->LUMO (62%)**, H-2->L+1 (27%)	π→π* Th→Tz
373	3.32	0.4827	H-3->LUMO (31%), **H-2->L+1 (53%)**	π→π* Tz-Th→Tz-Th
354	3.50	0.0009	**H-6->LUMO (96%)**	π→π* Tz-Th→Tz
352	3.52	0.3241	**H-5->LUMO (87%)**	π→π* Tz-Th→Tz
338	3.67	0.2086	**HOMO->L+2 (81%)**	π→π* TPA-Th→TPA-Th

[a] These values are used for the calculations shown in Figure 7.

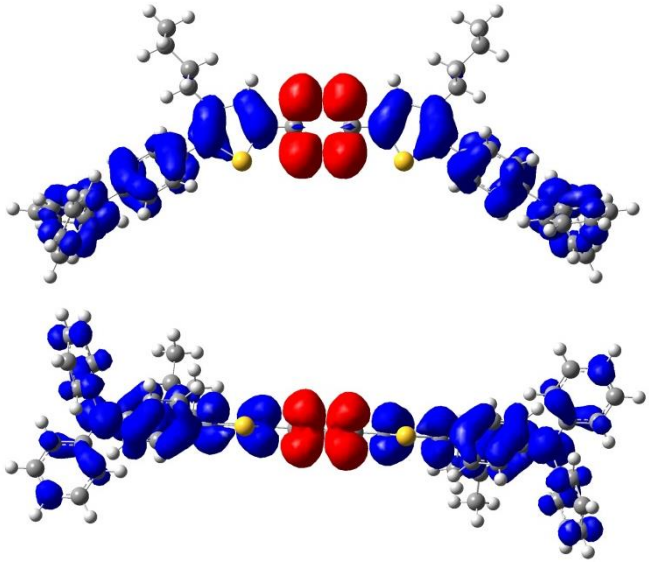


Figure S 16. Calculated electron density changes accompanying the first electronic excitation of 5. The blue and red lobes signify decreases and increases respectively in electron density accompanying the electronic transition. Their areas indicate the magnitude of the electron density change (isodensity=0.0004).

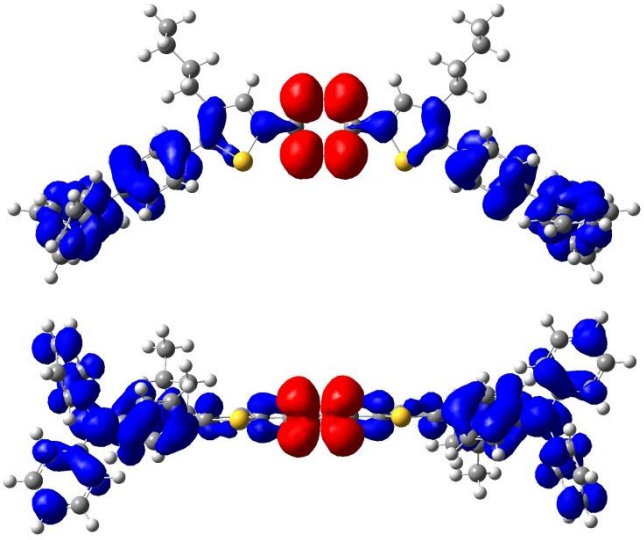


Figure S 17. Calculated electron density changes accompanying the third electronic excitation of 5. The blue and red lobes signify decreases and increases respectively in electron density accompanying the electronic transition. Their areas indicate the magnitude of the electron density change (isodensity=0.0004).

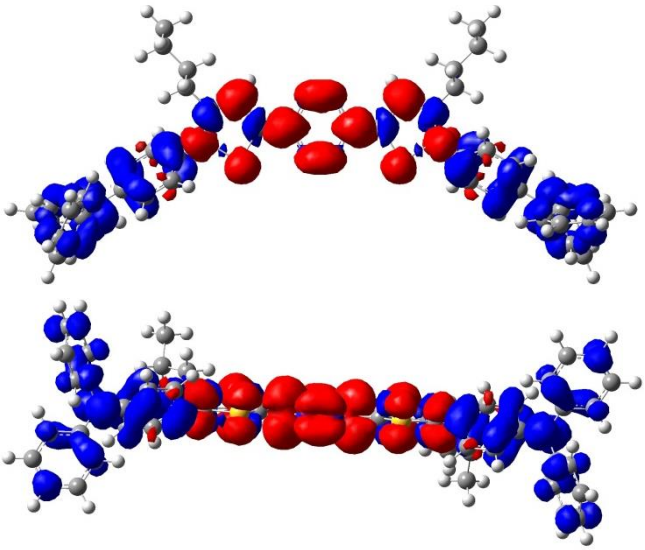


Figure S 18. Calculated electron density changes accompanying the fourth electronic excitation of 5. The blue and red lobes signify decreases and increases respectively in electron density accompanying the electronic transition. Their areas indicate the magnitude of the electron density change (isodensity=0.0004).

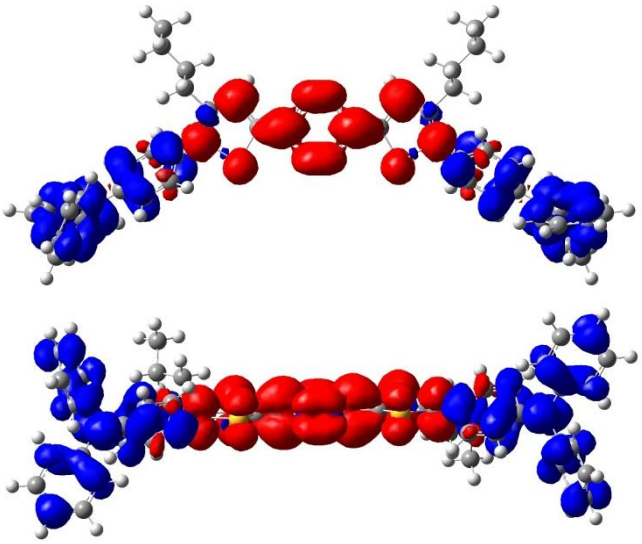


Figure S 19. Calculated electron density changes accompanying the fifth electronic excitation of 5. The blue and red lobes signify decreases and increases respectively in electron density accompanying the electronic transition. Their areas indicate the magnitude of the electron density change (isodensity=0.0004).

Table S 11. Atomic coordinates of compound **1** after geometry optimization

Number	Atomic number	X	Y	Z
1	6	-1.314592	-0.000084	-0.000019
2	6	1.314596	0.000052	-0.000018
3	7	-0.676837	0.001361	1.202253
4	7	0.676841	-0.001279	1.202253
5	7	-0.676837	-0.001403	-1.20229
6	7	0.676842	0.001333	-1.202289
7	6	-2.778399	-0.000072	-0.000018
8	6	-3.486581	-0.026933	-1.212032
9	6	-3.486578	0.026796	1.211997
10	6	-4.875403	-0.028405	-1.20886
11	1	-2.93016	-0.03665	-2.139849
12	6	-4.8754	0.028281	1.208829
13	1	-2.930155	0.036504	2.139814
14	6	-5.596919	-0.000057	-0.000015
15	1	-5.414898	-0.022785	-2.148466
16	1	-5.414893	0.02266	2.148436
17	6	2.778403	0.000031	-0.000018
18	6	3.486583	-0.026765	1.211999
19	6	3.486585	0.026807	-1.212034
20	6	4.875406	-0.028258	1.208829
21	1	2.930162	-0.036411	2.139816
22	6	4.875407	0.028271	-1.208863
23	1	2.930164	0.036467	-2.139851
24	6	5.596923	0	-0.000017
25	1	5.414897	-0.022584	2.148436
26	1	5.4149	0.022583	-2.14847
27	6	-7.079631	-0.000043	-0.000013
28	6	-7.805173	0.802903	0.897366
29	6	-7.805198	-0.802972	-0.897387
30	6	-9.195067	0.802336	0.902493
31	1	-7.271594	1.445122	1.588534
32	6	-9.195091	-0.802371	-0.902507
33	1	-7.271638	-1.445206	-1.588557
34	6	-9.915225	-0.000009	-0.000005
35	1	-9.734886	1.430298	1.599003
36	1	-9.734929	-1.430322	-1.599011
37	7	-11.338336	0.000009	0
38	6	-12.056375	1.214697	0.233375
39	6	-12.056418	-1.214655	-0.233356
40	6	-11.623446	2.420503	-0.342306
41	6	-13.20791	1.219012	1.037377
42	6	-11.623476	-2.420489	0.342255
43	6	-13.208013	-1.218918	-1.037274
44	6	-12.322442	3.603098	-0.108211
45	1	-10.739922	2.421429	-0.967467
46	6	-13.911719	2.402629	1.251897
47	1	-13.544027	0.292637	1.484798

48	6	-12.322519	-3.60306	0.108176
49	1	-10.739907	-2.421459	0.967352
50	6	-13.911866	-2.40251	-1.251778
51	1	-13.54414	-0.292521	-1.484643
52	6	-13.472337	3.602003	0.685581
53	1	-11.974931	4.525307	-0.559617
54	1	-14.798683	2.389148	1.874892
55	6	-13.472473	-3.601913	-0.68553
56	1	-11.974997	-4.525291	0.559528
57	1	-14.798876	-2.388988	-1.874707
58	1	-14.017694	4.521634	0.859928
59	1	-14.017866	-4.521525	-0.859866
60	6	7.079636	-0.000007	-0.000014
61	6	7.805187	-0.802913	0.897393
62	6	7.805192	0.802898	-0.897419
63	6	9.195081	-0.802325	0.902522
64	1	7.271617	-1.445117	1.588581
65	6	9.195086	0.802314	-0.902537
66	1	7.271625	1.445097	-1.588615
67	6	9.915228	-0.000003	-0.000003
68	1	9.734908	-1.430257	1.599053
69	1	9.734917	1.430244	-1.599067
70	7	11.338342	0.000001	0.000005
71	6	12.0564	-1.214672	0.233382
72	6	12.056394	1.21468	-0.233362
73	6	11.623449	-2.420503	-0.342229
74	6	13.207979	-1.218951	1.037324
75	6	11.623437	2.420504	0.342262
76	6	13.207971	1.218974	-1.037305
77	6	12.322465	-3.603085	-0.108126
78	1	10.739893	-2.421461	-0.967344
79	6	13.911806	-2.402555	1.251852
80	1	13.544114	-0.292558	1.484694
81	6	12.322447	3.603091	0.108172
82	1	10.739881	2.42145	0.967378
83	6	13.911793	2.402585	-1.25182
84	1	13.544112	0.292588	-1.484686
85	6	13.472401	-3.601954	0.685605
86	1	11.974934	-4.525312	-0.559478
87	1	14.798802	-2.389045	1.8748
88	6	13.472383	3.601974	-0.685559
89	1	11.974913	4.525312	0.559536
90	1	14.798789	2.389085	-1.874769
91	1	14.017774	-4.521575	0.859959
92	1	14.017751	4.5216	-0.859903

Number of imaginary frequencies: 0

Table S 12. Atomic coordinates of compound **2** after geometry optimization

Number	**Atomic number**	**X**	**Y**	**Z**

1	6	-2.931521	-0.000079	-0.000011
2	6	-5.560709	0.000055	0.000018
3	7	-3.569275	0.297177	-1.164958
4	7	-4.922952	0.29462	-1.165609
5	7	-3.569278	-0.297212	1.164964
6	7	-4.922958	-0.294559	1.165634
7	6	-1.467714	-0.000069	-0.000007
8	6	-0.759534	-0.324357	1.168129
9	6	-0.759533	0.324225	-1.168139
10	6	0.629288	-0.325005	1.164694
11	1	-1.315956	-0.562092	2.065023
12	6	0.629289	0.324883	-1.164701
13	1	-1.315955	0.561952	-2.065037
14	6	1.350806	-0.000056	-0.000002
15	1	1.168781	-0.550777	2.076789
16	1	1.168783	0.550653	-2.076797
17	6	-7.024516	0.000036	0.000011
18	6	-7.732694	0.272318	-1.181331
19	6	-7.7327	-0.272263	1.181345
20	6	-9.121517	0.270093	-1.178627
21	1	-7.176272	0.491286	-2.08299
22	6	-9.121522	-0.270062	1.17863
23	1	-7.176281	-0.491217	2.083009
24	6	-9.843036	0.000009	-0.000001
25	1	-9.661007	0.506812	-2.087945
26	1	-9.661016	-0.506794	2.087943
27	6	2.833518	-0.000044	0.000001
28	6	3.559062	0.999037	-0.672192
29	6	3.559083	-0.999109	0.672197
30	6	4.948956	0.999748	-0.677299
31	1	3.025485	1.79159	-1.18407
32	6	4.948976	-0.999788	0.677309
33	1	3.025521	-1.791677	1.184072
34	6	5.669112	-0.000012	0.000006
35	1	5.488776	1.779797	-1.197862
36	1	5.488813	-1.779826	1.19787
37	7	7.092223	0.000005	0.000007
38	6	7.810263	1.234769	0.072721
39	6	7.810304	-1.234732	-0.072715
40	6	7.377334	2.261833	0.927423
41	6	8.9618	1.436799	-0.705494
42	6	7.377362	-2.26184	-0.927359
43	6	8.961897	-1.436694	0.705434
44	6	8.076331	3.465668	0.991541
45	1	6.493809	2.108891	1.533587
46	6	9.665609	2.636808	-0.622153
47	1	9.297916	0.649012	-1.367119
48	6	8.076403	-3.465649	-0.991484
49	1	6.493794	-2.108955	-1.533474
50	6	9.665749	-2.636676	0.622084

51	1	9.298025	-0.648873	1.367014
52	6	9.226227	3.659941	0.221891
53	1	7.72882	4.248437	1.656003
54	1	10.552575	2.777047	-1.229306
55	6	9.226357	-3.659854	-0.221902
56	1	7.728882	-4.248452	-1.6559
57	1	10.552758	-2.776861	1.229186
58	1	9.771585	4.594196	0.279208
59	1	9.771748	-4.594088	-0.279223
60	35	-11.753036	0.000004	-0.00001

Number of imaginary frequencies: 0

Table S 13. Atomic coordinates of compound **3** after geometry optimization

Number	**Atomic number**	**X**	**Y**	**Z**
1	6	1.032935	-0.314396	0.747203
2	6	-1.039865	0.107116	-0.812768
3	7	-0.20792	-0.460006	1.283818
4	7	-1.276146	-0.2418	0.480095
5	7	1.269236	0.03482	-0.545331
6	7	0.200625	0.250915	-1.349906
7	6	2.189533	-0.544198	1.621313
8	6	3.487163	-0.397212	1.114312
9	6	1.992783	-0.916388	2.959851
10	6	4.604343	-0.609732	1.93307
11	1	3.609	-0.136004	0.071519
12	6	3.098426	-1.133838	3.77727
13	1	0.983267	-1.024926	3.332105
14	6	4.391015	-0.979591	3.274481
15	1	2.954685	-1.411457	4.814791
16	1	5.243566	-1.118806	3.928768
17	6	-2.197428	0.347776	-1.682666
18	6	-3.494597	0.220419	-1.168654
19	6	-2.00309	0.69836	-3.0274
20	6	-4.611282	0.447444	-1.983116
21	1	-3.617616	-0.074847	-0.135074
22	6	-3.109471	0.920776	-3.842709
23	1	-0.994003	0.79112	-3.405189
24	6	-4.401687	0.800879	-3.328988
25	1	-2.966462	1.200647	-4.879719
26	1	-5.257101	1.003894	-3.96277
27	6	5.981042	-0.438301	1.401107
28	6	7.028148	-1.284851	1.803251
29	6	6.280034	0.58011	0.479606
30	6	8.320463	-1.114333	1.320195
31	1	6.824215	-2.096641	2.491889
32	6	7.566475	0.747037	-0.019368
33	1	5.496441	1.257272	0.160196
34	6	8.613128	-0.09367	0.398489
35	1	9.111551	-1.777715	1.643848

36	1	7.773687	1.538393	-0.727538
37	7	9.934259	0.081885	-0.099455
38	6	10.773167	-1.054389	-0.329396
39	6	10.437764	1.393102	-0.36812
40	6	10.260044	-2.208337	-0.943345
41	6	12.123846	-1.029172	0.053249
42	6	10.163624	2.458125	0.505907
43	6	11.221005	1.633788	-1.50867
44	6	11.080349	-3.314401	-1.158684
45	1	9.220593	-2.23006	-1.24443
46	6	12.942492	-2.132345	-0.18196
47	1	12.521571	-0.142108	0.529086
48	6	10.651891	3.734888	0.234866
49	1	9.566672	2.277171	1.390417
50	6	11.720481	2.90969	-1.76329
51	1	11.433246	0.816645	-2.185807
52	6	12.426139	-3.282605	-0.784135
53	1	10.669424	-4.197856	-1.633705
54	1	13.98334	-2.097245	0.118742
55	6	11.435681	3.968988	-0.897806
56	1	10.430393	4.545899	0.919166
57	1	12.322785	3.078756	-2.648541
58	1	13.062991	-4.141285	-0.95933
59	1	11.819061	4.961297	-1.10248
60	6	-5.987384	0.325136	-1.435697
61	6	-7.014006	-0.280227	-2.179624
62	6	-6.303033	0.817181	-0.15806
63	6	-8.30592	-0.380325	-1.675073
64	1	-6.793713	-0.686214	-3.160321
65	6	-7.589178	0.707005	0.358408
66	1	-5.532552	1.299676	0.43222
67	6	-8.615156	0.110394	-0.394794
68	1	-9.083225	-0.850206	-2.263205
69	1	-7.811918	1.092487	1.344661
70	7	-9.936654	0.006234	0.125796
71	6	-10.724385	-1.156404	-0.143206
72	6	-10.482353	1.065215	0.91628
73	6	-10.146237	-2.435862	-0.102665
74	6	-12.090252	-1.036562	-0.447544
75	6	-10.256402	2.406682	0.566427
76	6	-11.254728	0.78005	2.05423
77	6	-10.916951	-3.565585	-0.370876
78	1	-9.095452	-2.534697	0.137306
79	6	-12.858166	-2.172437	-0.697168
80	1	-12.540066	-0.052766	-0.482709
81	6	-10.782437	3.435746	1.345024
82	1	-9.665984	2.631883	-0.312219
83	6	-11.792192	1.814733	2.817556
84	1	-11.429451	-0.25185	2.329905
85	6	-12.277306	-3.442789	-0.66529

86	1	-10.455138	-4.545633	-0.33521
87	1	-13.911015	-2.062445	-0.930611
88	6	-11.556514	3.147939	2.47213
89	1	-10.597838	4.465593	1.061474
90	1	-12.385377	1.57729	3.693242
91	1	-12.875453	-4.323343	-0.866319
92	1	-11.969655	3.949978	3.071787

Number of imaginary frequencies: 0

Table S 14. Atomic coordinates of compound **4** after geometry optimization

Number	Atomic number	X	Y	Z
1	6	-4.8032	-0.197053	0.07026
2	6	-2.618077	1.164227	-0.448011
3	7	-3.609601	-0.811875	0.275239
4	7	-2.481797	-0.110383	0.007047
5	7	-4.941305	1.07218	-0.393507
6	7	-3.814758	1.775458	-0.660343
7	6	-6.024261	-0.955768	0.368459
8	6	-7.277485	-0.360337	0.16427
9	6	-5.939994	-2.267948	0.855306
10	6	-8.428415	-1.076812	0.446365
11	1	-7.327862	0.65127	-0.211287
12	6	-7.10781	-2.972742	1.134004
13	1	-4.964069	-2.70865	1.005544
14	6	-8.356098	-2.379573	0.9303
15	1	-7.053116	-3.98675	1.510857
16	1	-9.267	-2.921922	1.144638
17	6	-1.397762	1.928236	-0.729376
18	6	-0.143055	1.340801	-0.51906
19	6	-1.489691	3.249128	-1.194457
20	6	1.033016	2.058276	-0.772218
21	1	-0.099154	0.32961	-0.136768
22	6	-0.323956	3.967482	-1.445732
23	1	-2.467202	3.685001	-1.34938
24	6	0.925874	3.381214	-1.23991
25	1	-0.387086	4.984876	-1.813123
26	1	1.828106	3.938637	-1.463043
27	6	2.36359	1.435081	-0.550447
28	6	3.414869	2.160634	0.034676
29	6	2.608515	0.100627	-0.915539
30	6	4.661641	1.581369	0.242292
31	1	3.247813	3.186237	0.343394
32	6	3.849023	-0.488692	-0.6991
33	1	1.819179	-0.477515	-1.381943
34	6	4.898871	0.243344	-0.11769
35	1	5.457975	2.156191	0.696464
36	1	4.01806	-1.518014	-0.986531
37	7	6.170939	-0.355972	0.10379

38	6	6.919254	-0.038703	1.280504
39	6	6.699752	-1.290769	-0.840736
40	6	6.276836	0.082356	2.523734
41	6	8.308847	0.151989	1.211038
42	6	6.579242	-1.056346	-2.220322
43	6	7.35068	-2.455309	-0.402319
44	6	7.008956	0.398568	3.666532
45	1	5.207028	-0.07035	2.583958
46	6	9.036677	0.449798	2.36172
47	1	8.80775	0.062388	0.254761
48	6	7.088812	-1.973786	-3.137255
49	1	6.083613	-0.157225	-2.562946
50	6	7.872995	-3.359365	-1.325461
51	1	7.443991	-2.640417	0.65989
52	6	8.392479	0.580146	3.594786
53	1	6.497986	0.488463	4.618295
54	1	10.108737	0.593806	2.2912
55	6	7.741804	-3.128043	-2.697151
56	1	6.987124	-1.778569	-4.198654
57	1	8.372131	-4.253913	-0.970984
58	1	8.959977	0.81878	4.486169
59	1	8.142674	-3.836175	-3.412291
60	35	-10.154645	-0.261823	0.165412

Number of imaginary frequencies: 0

Table S 15. Atomic coordinates of compound **5** after geometry optimization

Number	Atomic number	X	Y	Z
1	6	1.309168	1.647066	0.030112
2	6	-1.309143	1.647067	-0.029982
3	7	0.675304	2.858293	0.015978
4	7	-0.675275	2.858294	-0.016039
5	7	0.675055	0.439747	0.015613
6	7	-0.67504	0.439747	-0.015207
7	6	2.739763	1.645778	0.06305
8	6	3.583642	2.721019	0.081012
9	16	3.646052	0.08735	0.088475
10	6	4.9756	2.388579	0.108079
11	1	3.204786	3.733708	0.063363
12	6	5.206016	1.029524	0.121055
13	6	-2.739733	1.64578	-0.063011
14	6	-3.583619	2.72101	-0.081112
15	16	-3.646019	0.087335	-0.088248
16	6	-4.975576	2.388559	-0.108246
17	1	-3.204775	3.733705	-0.063541
18	6	-5.20598	1.029501	-0.121096
19	6	6.470602	0.291983	0.142355
20	6	7.478666	0.598696	1.07579
21	6	6.704606	-0.767127	-0.7551
22	6	8.680727	-0.098245	1.08903

23	1	7.306225	1.380225	1.805568
24	6	7.898009	-1.476827	-0.73422
25	1	5.93723	-1.028901	-1.474257
26	6	8.91348	-1.149522	0.1834
27	1	9.444195	0.155248	1.81236
28	1	8.056616	-2.288286	-1.431877
29	7	10.138514	-1.86725	0.201358
30	6	10.820983	-2.098954	1.438871
31	6	10.705438	-2.3649	-1.01479
32	6	10.109334	-2.495269	2.582469
33	6	12.213186	-1.940049	1.522073
34	6	11.278525	-3.645794	-1.058604
35	6	10.705026	-1.577952	-2.177942
36	6	10.77794	-2.713703	3.785737
37	1	9.036705	-2.626551	2.519815
38	6	12.877085	-2.177351	2.724434
39	1	12.764185	-1.634649	0.641933
40	6	11.842064	-4.123954	-2.240255
41	1	11.279075	-4.255462	-0.164358
42	6	11.254012	-2.070298	-3.360522
43	1	10.271475	-0.586673	-2.147075
44	6	12.164587	-2.560008	3.863808
45	1	10.21499	-3.01884	4.660299
46	1	13.952446	-2.050442	2.773501
47	6	11.829043	-3.343101	-3.398894
48	1	12.280042	-5.115285	-2.258447
49	1	11.24497	-1.451267	-4.250283
50	1	12.682441	-2.737302	4.798667
51	1	12.260926	-3.720668	-4.317832
52	6	-6.470561	0.291955	-0.142377
53	6	-7.478542	0.598498	-1.075964
54	6	-6.704648	-0.766988	0.755248
55	6	-8.680601	-0.098444	-1.089184
56	1	-7.306032	1.379888	-1.805874
57	6	-7.898053	-1.476687	0.734396
58	1	-5.937341	-1.02863	1.474528
59	6	-8.91344	-1.149549	-0.183373
60	1	-9.444006	0.154917	-1.812627
61	1	-8.056726	-2.288014	1.432192
62	7	-10.138475	-1.867275	-0.201299
63	6	-10.820866	-2.099176	-1.438818
64	6	-10.705487	-2.364723	1.014894
65	6	-10.109144	-2.495669	-2.582309
66	6	-12.213063	-1.94028	-1.522134
67	6	-11.278527	-3.64563	1.058889
68	6	-10.705209	-1.577562	2.177901
69	6	-10.777674	-2.714295	-3.785584
70	1	-9.036519	-2.626941	-2.519566
71	6	-12.876886	-2.177776	-2.7245
72	1	-12.764119	-1.634738	-0.64208

73	6	-11.842155	-4.123597	2.240577
74	1	-11.278974	-4.255461	0.164755
75	6	-11.254282	-2.069714	3.360522
76	1	-10.271691	-0.586273	2.146893
77	6	-12.164317	-2.560615	-3.863766
78	1	-10.214669	-3.019571	-4.660062
79	1	-13.952245	-2.050874	-2.773654
80	6	-11.829268	-3.342532	3.399074
81	1	-12.280095	-5.114942	2.258911
82	1	-11.245344	-1.450521	4.25017
83	1	-12.682111	-2.738059	-4.79863
84	1	-12.261218	-3.719949	4.318042
85	6	6.053252	3.45101	0.026585
86	6	5.996821	4.229746	-1.315112
87	1	7.037634	2.984354	0.120274
88	1	5.937415	4.159908	0.858005
89	6	7.092492	5.313635	-1.406306
90	1	6.113225	3.51739	-2.141227
91	1	5.010863	4.699346	-1.425589
92	6	7.034428	6.084079	-2.742991
93	1	6.975876	6.017183	-0.570932
94	1	8.077273	4.840261	-1.296774
95	1	7.815851	6.850502	-2.790407
96	1	7.17348	5.399306	-3.587636
97	1	6.062384	6.577119	-2.860407
98	6	-6.053223	3.451011	-0.026915
99	6	-5.996999	4.229733	1.314806
100	1	-7.037597	2.984375	-0.12076
101	1	-5.937242	4.159917	-0.858308
102	6	-7.092649	5.313655	1.405821
103	1	-6.113569	3.517369	2.140889
104	1	-5.011045	4.699298	1.42546
105	6	-7.034812	6.084074	2.742531
106	1	-6.975859	6.017213	0.570481
107	1	-8.077426	4.840314	1.2961
108	1	-7.816185	6.850557	2.789791
109	1	-7.174098	5.399299	3.587136
110	1	-6.062755	6.577037	2.860162

Number of imaginary frequencies: 0

Table S 16. Atomic coordinates of compound **6** after geometry optimization

Number	**Atomic number**	**X**	**Y**	**Z**
1	6	4.473433	-0.207088	-0.044977
2	6	1.935054	0.416092	-0.18245
3	7	4.156434	1.092521	-0.317679
4	7	2.845927	1.414985	-0.389278
5	7	3.565232	-1.200385	0.168176
6	7	2.255955	-0.8808	0.097528

7	6	5.860029	-0.555103	0.023701
8	6	6.946875	0.255009	-0.149572
9	16	6.336227	-2.261699	0.376725
10	6	8.210552	-0.407952	-0.017222
11	1	6.834468	1.306405	-0.36839
12	6	8.054721	-1.736754	0.259281
13	6	0.547925	0.753204	-0.266107
14	6	-0.008149	1.974955	-0.527162
15	16	-0.711962	-0.513243	-0.021735
16	6	-1.438697	1.989436	-0.544044
17	1	0.606081	2.849229	-0.693856
18	6	-1.994232	0.751148	-0.300749
19	6	-3.400408	0.349775	-0.232418
20	6	-4.306212	0.691738	-1.254401
21	6	-3.881724	-0.419216	0.844019
22	6	-5.640584	0.31075	-1.187704
23	1	-3.95164	1.2462	-2.114629
24	6	-5.211176	-0.814911	0.906834
25	1	-3.199186	-0.704405	1.636122
26	6	-6.119096	-0.450401	-0.105037
27	1	-6.321097	0.585985	-1.982296
28	1	-5.5601	-1.407052	1.742215
29	7	-7.479774	-0.847541	-0.040258
30	6	-8.202769	-1.146581	-1.240361
31	6	-8.146919	-0.955223	1.221605
32	6	-7.615678	-1.922168	-2.252692
33	6	-9.512401	-0.672908	-1.415058
34	6	-9.00795	-2.033898	1.478201
35	6	-7.961059	0.020065	2.214696
36	6	-8.322624	-2.20519	-3.420214
37	1	-6.608372	-2.29494	-2.117829
38	6	-10.219363	-0.974591	-2.577811
39	1	-9.966865	-0.074392	-0.636128
40	6	-9.670159	-2.129752	2.700846
41	1	-9.153315	-2.787601	0.715171
42	6	-8.612922	-0.092222	3.441478
43	1	-7.304573	0.85816	2.018897
44	6	-9.628372	-1.73714	-3.588519
45	1	-7.856498	-2.805021	-4.193353
46	1	-11.230006	-0.602081	-2.69909
47	6	-9.473814	-1.163985	3.691246
48	1	-10.331218	-2.968964	2.884111
49	1	-8.458364	0.668151	4.198372
50	1	-10.177996	-1.96464	-4.493912
51	1	-9.984362	-1.245047	4.64322
52	6	9.563811	0.259644	-0.162395
53	6	9.506843	1.76912	-0.481872
54	1	10.124479	-0.252343	-0.956069
55	1	10.129111	0.113289	0.767937
56	6	10.920587	2.376218	-0.615346

57	1	8.957725	1.928444	-1.419105
58	1	8.964436	2.29527	0.31461
59	6	10.876187	3.886327	-0.931634
60	1	11.471783	2.211874	0.320014
61	1	11.464852	1.849343	-1.410238
62	1	11.887175	4.298571	-1.020231
63	1	10.348559	4.067249	-1.875303
64	1	10.352305	4.430942	-0.137547
65	6	-2.222559	3.276197	-0.706282
66	6	-2.008326	4.23309	0.497241
67	1	-3.289106	3.0508	-0.789987
68	1	-1.912598	3.784321	-1.629544
69	6	-2.797448	5.551195	0.342418
70	1	-2.323306	3.720517	1.414579
71	1	-0.939016	4.458894	0.599973
72	6	-2.587621	6.495546	1.545589
73	1	-2.481961	6.055426	-0.58089
74	1	-3.865911	5.320433	0.237539
75	1	-3.155491	7.424146	1.42128
76	1	-2.916267	6.013661	2.473738
77	1	-1.527484	6.753416	1.652198
78	35	9.44413	-3.006948	0.514011

Number of imaginary frequencies: 0