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Supporting Information

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Transforming Surface Coordination Polymers to Covalent Surface Polymers: Linked Poly-Condensed Aromatics via Oligomerisation of N-Heterocyclic Carbene Intermediates

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Contents:

SI.1 - XPS measurements on TAPP/Cu(111)

The XPS spectra were recorded at the Paul Scherrer Institute on a SPECS Phoibos 150 hemispherical electron energy analyzer using an Al-K$_\alpha$ X-ray source. After each XPS-measurement, the sample was newly prepared to prevent measuring errors due to possible radiation damage of the molecules. For the same reason care has been taken to assure that the spectra did not change during one measurement. The successful preparation of the pores was checked by LEED while the chains were checked by STM.

Figure 1 shows the N1s XPS spectra after background subtraction. The spectrum recorded after the thermal generation of the **TAPP** chains is broadened and slightly shifted towards lower energies compared to the spectrum obtained from a sample bearing the porous surface coordination polymer.

For a quantitative analysis a Gaussian shaped peak was fitted to the spectrum of the porous network structure, exhibiting an energy of 398.74 eV and a peak width of 1.16 eV (Figure 1a). In contrast, besides this maximum, a second peak is expected for the chain structure due to the inequivalence of the N-atoms in the polymer. Therefore, two peaks were fitted to the N1s spectrum of the chains (Figure 1b). The energy of one peak and the width of both peaks were set to the values determined for the pores in order to reduce the number of free parameters in the fit process. The energy of the second peak corresponds to 398.10 eV which results in a chemical shift of 0.6 eV between both N-atom environments.
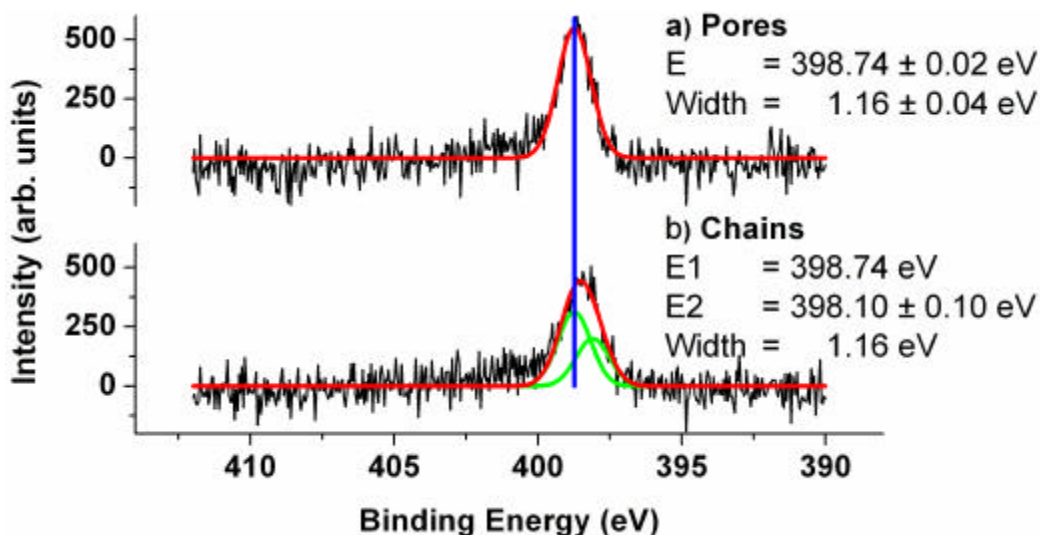
Figure 1:
XPS spectra of the N1s peak for TAPP on Cu(111) after background subtraction. a) The spectrum of the porous network was fitted by one Gaussian shaped peak. The position of the peak, which is highlighted by the blue line, is at an energy of 398.74 eV. b) The peak of the chains is broadened and slightly shifted towards lower energies. It was fitted by two Gaussian shaped peaks (green curves). The energy of one peak and the width of both peaks were set to the values calculated for the porous network.

SI.2 - LEED on TAPP/Cu(111)

LEED measurements were performed to determine the dimension of the unit cell of the porous TAPP network accurately. After the deposition of TAPP onto atomically clean Cu(111) surfaces, the sample was annealed at 150°C. The LEED patterns were taken from samples held at room temperature (Figure 2a, c and d). The sample was slightly tilted with respect to normal incidence to provide a better visibility of the diffraction spots of first order that would otherwise interfere with the electron gun. The analysis of the LEED pattern supports a commensurate superstructure of the molecular ad-layer on the substrate. The matrix of the molecular ad-layer (Park and Madden) was found to be:

$$\begin{pmatrix} 8 & 5 \\ -1 & 6 \end{pmatrix}.$$

The software LEEDpat 2.1 [1] was used to simulate the LEED pattern (Figure 2b). Beside the fact that the LEED pattern is very well reproduced by the simulation using the above matrix there are two other points that strongly support a commensurate ad-layer: On the one hand very large homogenous islands of TAPP could be observed on the Cu surface (larger than 100 nm^2 in size). On the other hand, the molecular LEED-pattern around the (00)-spot (Figure 2a, c) is reproduced at the first order LEED-spot of the Cu substrate (Figure 2d).

We note that the molecular layer is commensurate with the underlying Cu substrate which does not imply that the threefold symmetry of the underlying substrate has to result in a threefold symmetry of the molecular layer. For example, for the case of PTCDA on Ag(111) an

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[1] K. Hermann and M. A. van Hove, LEED pattern simulator LEEDpat Version 2.1 (2006)

almost rectangular unit cell is observed which is commensurate to the Ag substrate (K. Glöckler et al., *Surf. Sci.* **1998,** *405*, 1).

The information on the dimensions of the unit cell and the structural data of **TAPP** (obtained by single crystal X-ray diffraction) itself were used to calculate the overall N-Cu-N distance to 4Å.
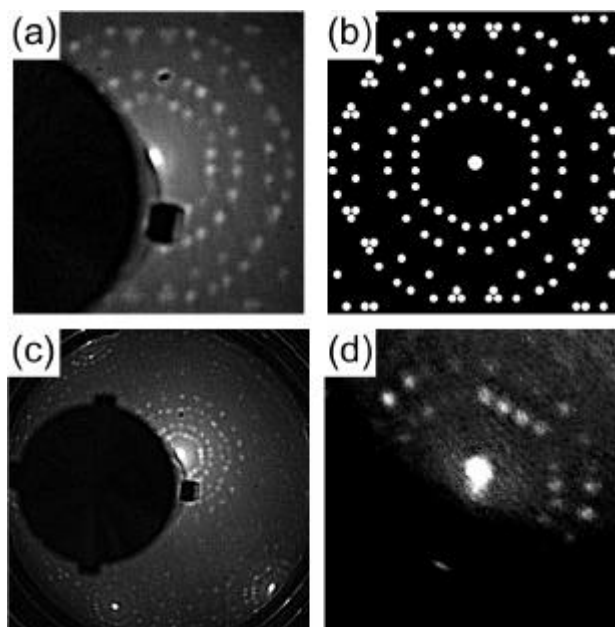

Figure 2: LEED patterns of the porous TAPP network on Cu(111) at an electron beam energy of (a) 65 eV and (c) 29.5 eV. d) Zoom-in on one of the first order spots of the Cu substrate. The LEED pattern was taken at 52 eV. b) LEED pattern simulated for the molecular layer on the Cu(111) surface shown for comparison.

SI.3 – STM manipulation Experiments

The manipulation experiments were carried out at an STM temperature of 5 K (a bath cryostat is used). This low temperature ensures that the thermal drift is reduced to a minimum and tip and sample do (almost) not move with respect to each other (a drift of $2.5*10^{-4}$ Å/s was determined for the z-signal if the tip is kept in place laterally).
In our case, for the manipulation of the chains the distance between tip and sample was lowered by 0.7 nm. The closer proximity of the tip causes an interaction between tip and molecular chain, what in most cases was found to be repulsive (the chain was pushed aside).
To ensure that always the same conditions for the manipulation are met the procedure was performed in constant height mode. It should be noted, that no lateral movement of the tip in x- or y-direction was performed. Thus, no *lateral manipulation* was performed. For more information about manipulation with the STM tip, lateral manipulation in constant height and constant current mode see the review article by F. Moresco, *Phys. Rep.* **2004**, *399*, 175.

SI.4 - DFT-calculations:

All calculations were performed using the Gaussian 03 program.[2] The structures were optimized without symmetry constraints at the DFT/B3PW91 level using the 6-31g(d,p); 6-311g(d,p), sto-3g basis sets. Frequency calculations were performed to ensure the absence of any imaginary frequencies, and thus determining that the respective calculated structure was a minimum on the potential energy surface. As points of reference for comparison with the TAPP molecule, calculations on pyridine, pyrimidine as well as the respective carbene and its dimeric structures were performed.

The energy barrier for the polymerization of the TAPP molecule is the formation of the carbene structure. This energy barrier is 53,1 kcal/mol (6-31g(d,p) respectively 50,6 kcal/mol (6-311 g(d,p)) [see below]. The 6-311g(d,p) calculated energies for pyridine and pyrimidine revealed the respective energy barriers of 43,5 kcal/mol and 50,3 kcal/mol. These values are in good agreement with literature values for pyridine 47-50 kcal/mol performed by Koch, Schwarz and coworkers.[3]

B3PW91/6-311G(d,p)**

+43,5 kcal/mol   -62,6 kcal/mol

+50,3 kcal/mol   -88,7 kcal/mol

42,3 kcal/mol   72,6 kcal/mol
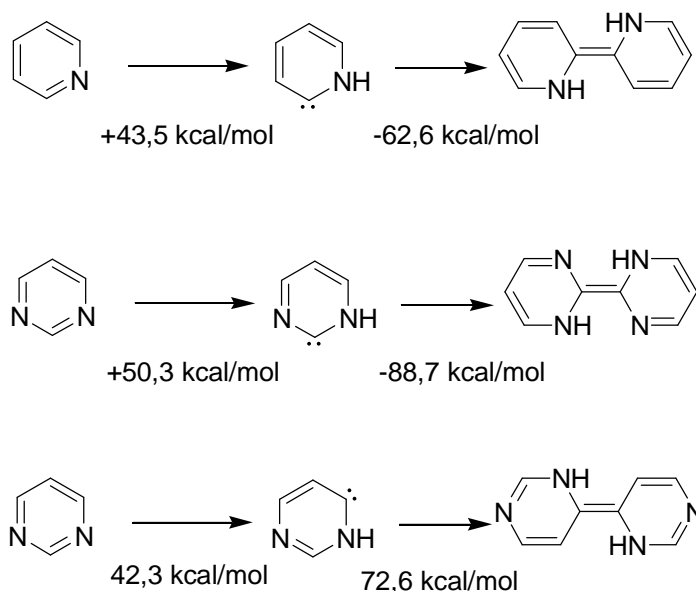
The dimerization reaction of two carbene units is exothernmic by 106,4 kcal /mol (B3PW91/6-31g(d,p) for the TAPP carbene, 62,6 kca/mol for pyridine carbene and 88,7 kcal/mol for the

[2] Gaussian 03, Revision B.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
[3] D. Lavorato, J. K. Terlouw, T. K. Dargel, W. Koch, G. A. McGibbon, H. Schwarz, *J. Am. Chem. Soc.* **1996**, *118*, 11898-11904.

pyrimidine carbene (each B3PW91/6-311g(d,p)**). The overall reaction along this pathway in the gasphase is therefore disfavored by 24,4 kcal/mol for pyridine, 11,9 kcal/mol for pyrimidine and approximately thermoneutral (slightly favored by 0.2 kcal/mol) for the dimerization of two TAPP units.

+53,1 kcal/mol   + 53,4 kcal/mol

2x   -106,4 kcal/mol
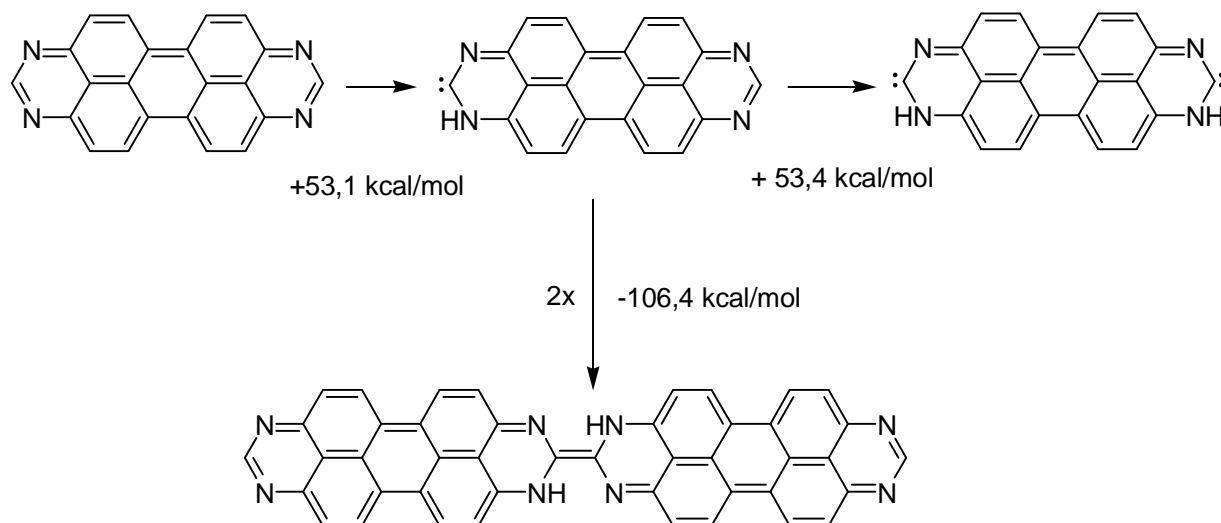
The energy balance becomes even more favorable for the trimerization of three TAPP molecules (18,6 kcal/mol). A tetramer could not be calculated at the 6-31g(d,p) level. However, in order to probe the qualitative trend, all molecules were remodelled with B3PW91/sto-3g and quadratical convergence criteria. The results are summarized in the graph below demonstrating the general trend of increasing stabilization upon going to higher oligomers.
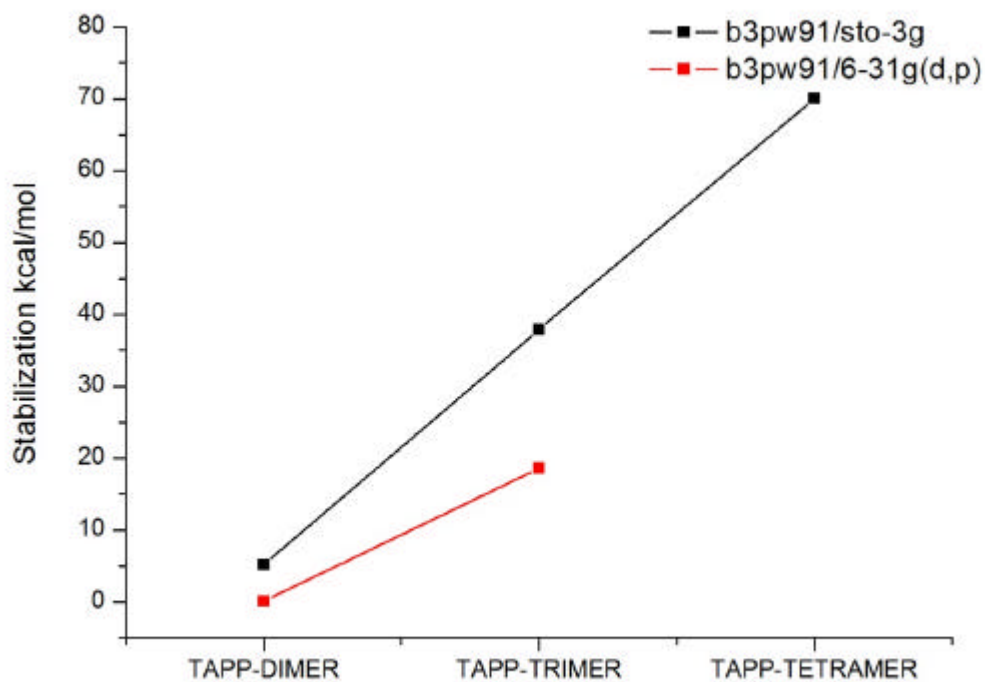
All calculated structures is completely planar. The calculated bond length of the newly formed double bond and the distance of the monomeric units are summarized in the table below.

	B3PW91 /	C=C Bond Length	Monomer Distance
Dimer	6-31g(d,p)	1,44	12,51
Dimer	Sto-3g	1,50	12,71
Trimer	Sto-3g	1,50	12,79
Tetramer	Sto-3g	1,50	12,78
Pyridine dimer	6-311g(d,p)	1,37	
Pyrimidine dimer	6-311g(s,p)	1,36	

Figures of the frontier orbitals of TAPP and its oligomers are depicted below:
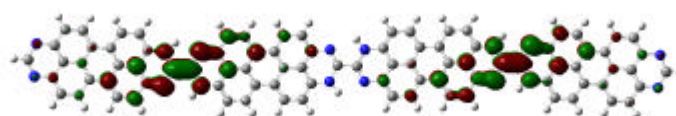
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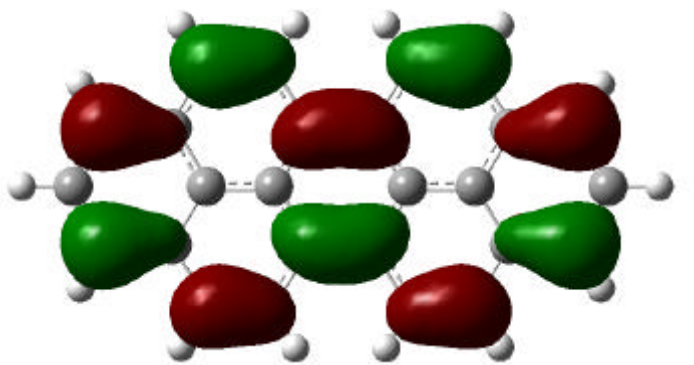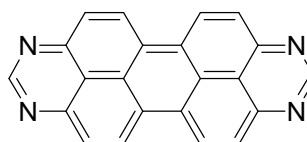
HOMO
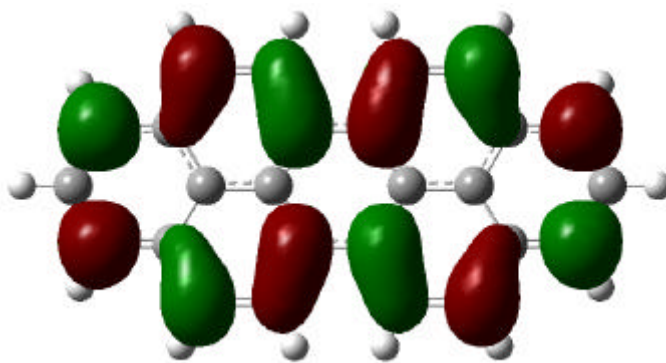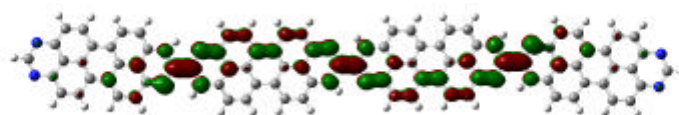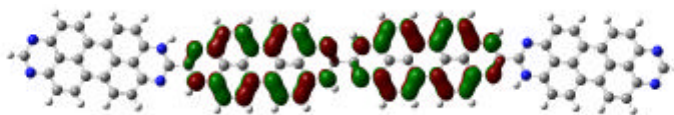

LUMO

B) DIMER:
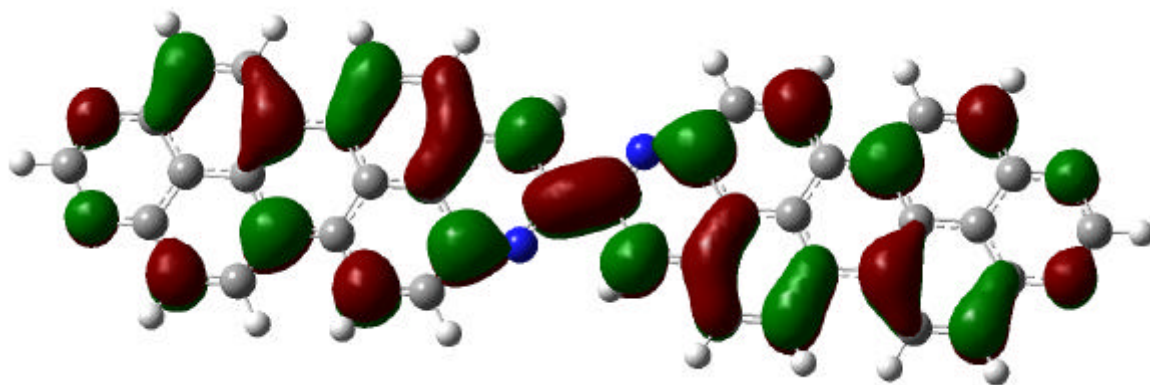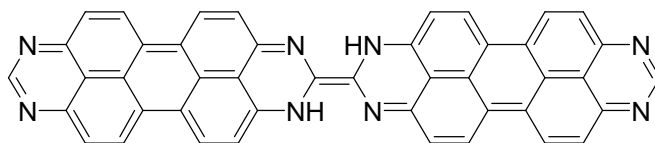
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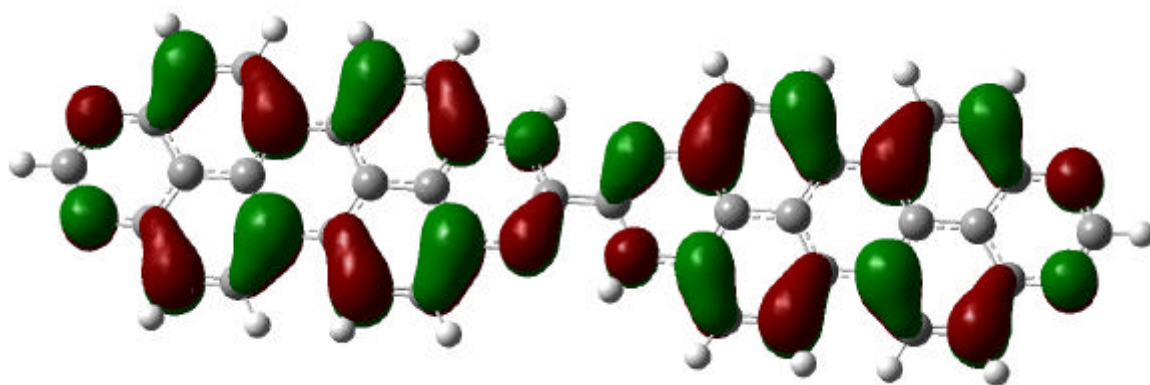
LUMO

C) TRIMER:
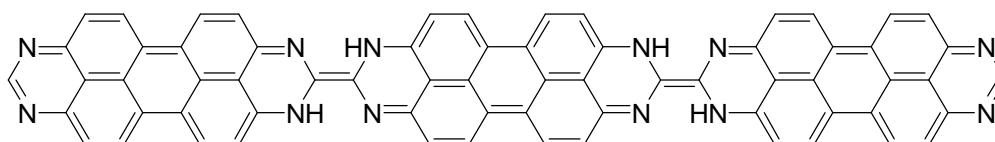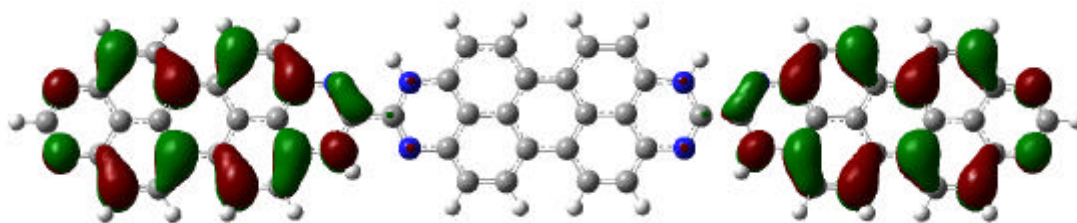
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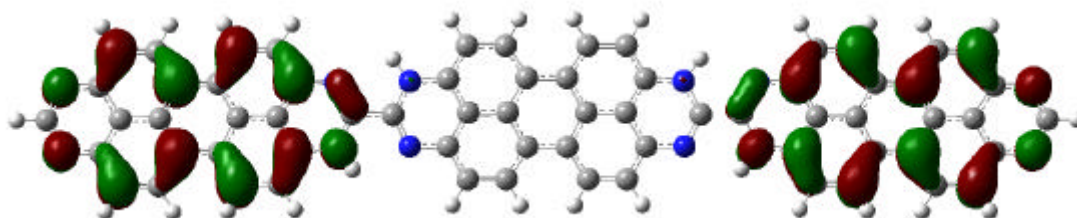
LUMO

D) TETRAMER
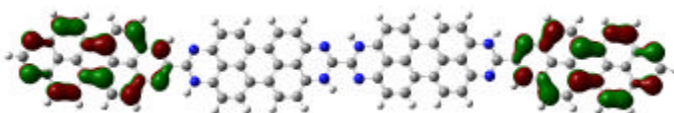
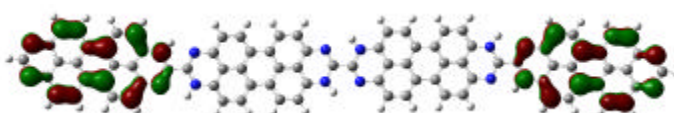**LUMO+4**
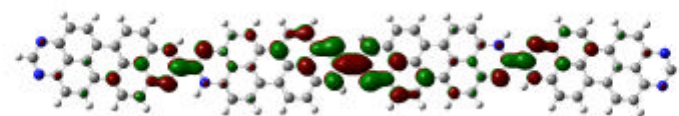
LUMO+3

LUMO+2

LUMO+1

LUMO

HOMO

HOMO-1

HOMO-2

HOMO-3

HOMO-4