

## Electronic structure and charge transfer excited states of endohedral trimetallic nitride $C_{80} (I_h)$ fullerenes-Zntetraphenyl porphyrin dyads

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Keywords:

- a) The exponents of the Gaussian basis functions used in this study are given in Table I.  
b) The comparison of the charge transfer excitation energy values obtained using our method and time dependent density functional theory method with range-corrected functionals and available experimental values for a set of organic donor-acceptor system are given in table II.

TABLE I: The Gaussian basis functions used for each atom is given below.

Atom	Number of primitives	Gaussian exponents
H	6	$0.77840 \times 10^2$ , $0.11534 \times 10^2$ , $0.26138 \times 10^1$ , $0.73216 \times 10^0$ , $0.73216 \times 10^0$ , $0.22838 \times 10^0$ , $0.74506 \times 10^{-1}$
C	12	$0.22213 \times 10^5$ , $0.33317 \times 10^4$ , $0.75790 \times 10^3$ , $0.21454 \times 10^3$ , $0.69924 \times 10^2$ , $0.25086 \times 10^2$ , $0.95910 \times 10^1$ , $0.38024 \times 10^1$ , $0.14891 \times 10^1$ , $0.57487 \times 10^0$ , $0.21494 \times 10^0$ , $0.77209 \times 10^{-1}$
N	13	$0.51750 \times 10^5$ , $0.78061 \times 10^4$ , $0.17858 \times 10^4$ , $0.50740 \times 10^3$ , $0.16585 \times 10^3$ , $0.59844 \times 10^2$ , $0.23134 \times 10^2$ , $0.94184 \times 10^1$ , $0.39417 \times 10^1$ , $0.16227 \times 10^1$ , $0.65266 \times 10^0$ , $0.25437 \times 10^0$ , $0.94111 \times 10^{-1}$
Sc	19	$0.15652 \times 10^7$ , $0.23534 \times 10^6$ , $0.53650 \times 10^5$ , $0.15207 \times 10^5$ , $0.49624 \times 10^4$ , $0.17915 \times 10^4$ , $0.69862 \times 10^3$ , $0.28935 \times 10^3$ , $0.12578 \times 10^3$ , $0.56804 \times 10^2$ , $0.26183 \times 10^2$ , $0.12231 \times 10^2$ , $0.57796 \times 10^1$ , $0.27308 \times 10^1$ , $0.12660 \times 10^1$ , $0.56756 \times 10^0$ , $0.23855 \times 10^0$ , $0.91083 \times 10^{-1}$ , $0.35242 \times 10^{-1}$
Zn	20	$0.50080 \times 10^7$ , $0.72276 \times 10^6$ , $0.16155 \times 10^6$ , $0.45310 \times 10^5$ , $0.14692 \times 10^5$ , $0.52826 \times 10^4$ , $0.20546 \times 10^4$ , $0.85038 \times 10^3$ , $0.37028 \times 10^3$ , $0.16797 \times 10^3$ , $0.78747 \times 10^2$ , $0.37707 \times 10^2$ , $0.18410 \times 10^2$ , $0.91174 \times 10^1$ , $0.44408 \times 10^1$ , $0.20866 \times 10^1$ , $0.94492 \times 10^0$ , $0.39820 \times 10^0$ , $0.15274 \times 10^0$ , $0.55405 \times 10^{-1}$
Y	23	$0.10462 \times 10^8$ , $0.17201 \times 10^7$ , $0.41811 \times 10^6$ , $0.12358 \times 10^6$ , $0.41543 \times 10^5$ , $0.15336 \times 10^5$ , $0.60882 \times 10^4$ , $0.25623 \times 10^4$ , $0.11316 \times 10^4$ , $0.52050 \times 10^3$ , $0.24775 \times 10^3$ , $0.12123 \times 10^3$ , $0.60611 \times 10^2$ , $0.30862 \times 10^2$ , $0.15880 \times 10^2$ , $0.80847 \times 10^1$ , $0.41002 \times 10^1$ , $0.20544 \times 10^1$ , $0.98327 \times 10^0$ , $0.45769 \times 10^0$ , $0.19977 \times 10^0$ , $0.80344 \times 10^{-1}$ , $0.32174 \times 10^{-1}$

TABLE II: The HOMO to LUMO charge transfer excitation energies in TCNE-hydrocarbon complexes[1], the C<sub>2</sub>H<sub>4</sub>-C<sub>2</sub>F<sub>4</sub>[2, 3] and the NH<sub>3</sub>-F<sub>2</sub>[3] molecules, and the pentacene-C<sub>60</sub> and the tetraphenyl porphyrin (TPP)-C<sub>60</sub> complexes. The numbers in the round bracket in the first column correspond to the distance between donor and acceptor unit. The asterisk and **(S)** indicate that the values are in gas-phase and in solution, respectively. A universal solvent correction of -0.3 eV is applied to both TDDFT and our numbers for the systems e through l. The experimental values for systems m through s are obtained by using the experimental gas-phase ionization energy and electron affinity in the Mulliken's formula  $E=IP-EA-1/R$ .

Label	TCNE-hydrocarbons	Singlet (eV)	TDDFT[1] (eV)	Expt. (eV)	Deviation
a	TCNE-benzene**	3.63	3.8	3.59	- -0.04
b	TCNE-naphtalene**	2.72	2.7	2.6	- -0.12
c	TCNE-toluene**	3.42	3.4	3.36	- -0.06
d	TCNE-xylene**	3.05	3	3.15	- 0.1
e	TCNE-anthracene(S)	1.65	1.82	1.73	0.08
f	TCNE-9-10-dimeth-anth(S)	1.34	1.77	1.44	0.1
g	TCNE-9-cmo-anth(S)	1.89	1.84	1.84	-0.05
h	TCNE-9f-10ch-anth (S)	2.03	1.96	1.96	-0.07
i	TCNE-9-form-anth(S)	2.0	1.95	1.9	-0.1
j	TCNE-9-meth-anth(S)	1.54	1.71	1.55	0.01
k	TCNE-9-chloro-anth(S)	1.76	1.82	1.74	-0.02
l	TCNE-9-cyano-anth(S)	1.72	2.03	2.01	-0.29
m	C <sub>2</sub> H <sub>4</sub> -C <sub>2</sub> F <sub>4</sub> (8Å)	10.5		12.7	- -0.2
n	C <sub>2</sub> H <sub>4</sub> -C <sub>2</sub> F <sub>4</sub> (25Å)	11.78		11.92	- -0.14
o	C <sub>2</sub> H <sub>4</sub> -C <sub>2</sub> F <sub>4</sub> (100Å)	12.2		12.36	- -0.16
p	NH <sub>3</sub> -F <sub>2</sub> (8 Å)	9.25		9.49	-0.24
q	pentacene-C <sub>60</sub> (20Å)	3.10		3.19	-0.09
r	pentacene-C <sub>60</sub> (100Å)	3.47		3.77	-0.3
s	TPP-C <sub>60</sub> (20Å)	3.27		3.30	-0.03

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- [1] T. Stein, L. Kronik, and R. Baer, Journal of the American Chemical Society **131**, 2818 (2009), 427PX Times Cited:62 Cited References Count:49.
- [2] Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, and K. Hirao, Journal of Chemical Physics **120**, 8425 (2004), 819EY Times Cited:350 Cited References Count:44.
- [3] Y. Zhao and D. G. Truhlar, Journal of Physical Chemistry A **110**, 13126 (2006), 113VK Times Cited:158 Cited References Count:63.