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Photoinduced Electron Transfer in Donor–Acceptor Nanosystems: A Theoretical Study

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1 Introduction

Donor-acceptor nanosystems are often used to mimic natural photosynthesis and in organic photovoltaic (OPV) devices.[1] Photoinduced electron transfer (PIET) is a crucial process for above applications and its deep understanding is therefore vital for designing new materials for solar energy conversion.[1] Both experimental and theoretical studies in this field are important and their close collaboration is essentially synergetic. Here we provide an example of such a collaborative research, where theory is used to explain experimental phenomena,[2,3] and suggest and predict properties of unknown nanosystems.[4]

2 Methods

PIET has been experimentally observed as charge-transfer (CT) bands in UV/vis spectra of systems described in 3.1 and 3.2. These bands are typically by factor of 10^3 less intensive than that of λ_{\max} . Thus we have studied excited states corresponding to CT states with methods calibrated to UV/vis spectra.

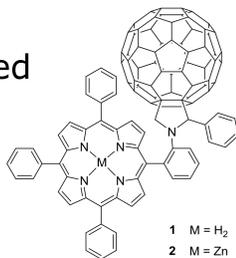
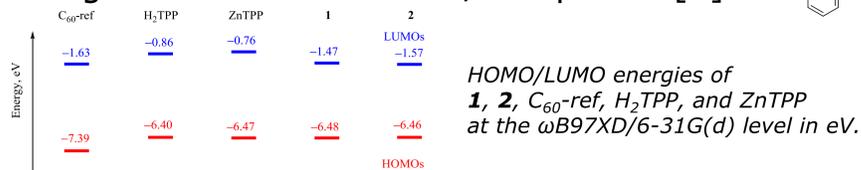
Used methods:

- Semiempirical CIS and UNO-CIS methods as implemented in VAMP 11.0, which are the fastest methods. UNO-CIS methods have advantage of automatically selecting orbitals for calculations.[5]
- SAOP/TZP as implemented in ADF 2012
- TD B3LYP/SVP as implemented in Gaussian 09

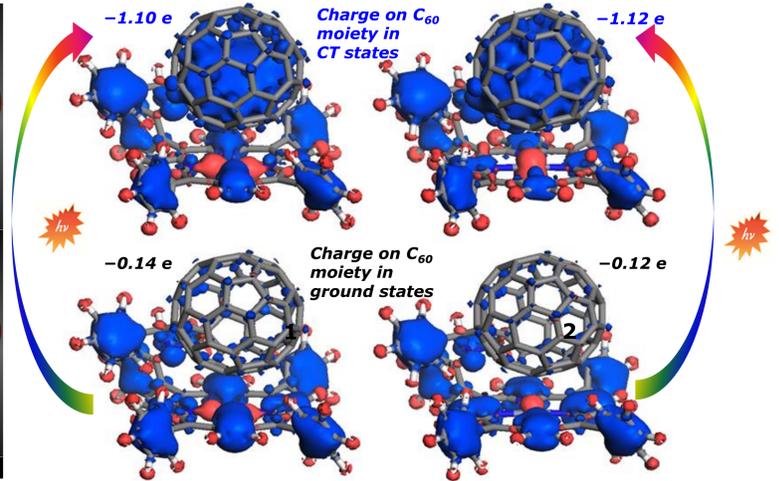
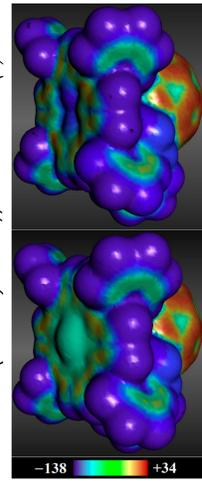
3 Results and Discussion

3.1 Explanation: Porphyrin-Fullerene Dyads

PM6 UNO-CIS calculations supported by SAOP/TZP calculations clearly demonstrated that “frozen” close proximity of donor (porphyrin) and acceptor (C_{60}) moieties is responsible for observed experimentally charge-transfer band in UV/vis spectra.[2]



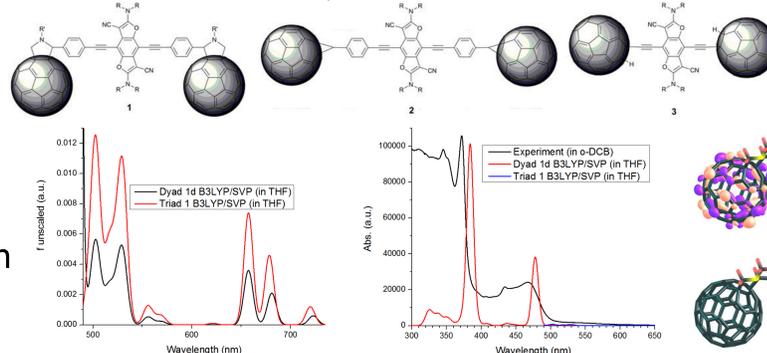
Local electron affinity (EA) isosurfaces of **1** (top) and **2** (bottom) at PM6// ω B97XD/6-31G(d)



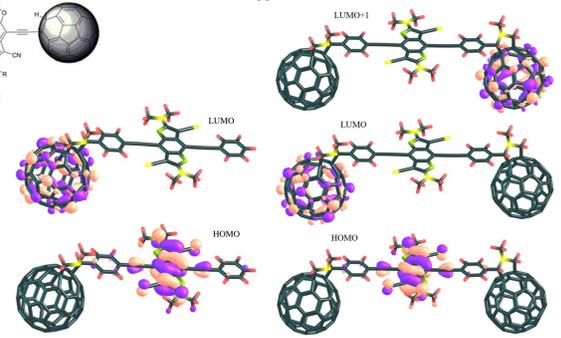
3.2 Explanation: Benzodifuran (BDF)- C_{60} Bumbbell-type Triads

TD B3LYP/SVP method appeared to be the best method among many others that we have tried to reproduce entire experimental UV/vis spectra, although one out of two C_{60} s was replaced with hydrogen to calculate respective dyads instead of triads. Excitations in dyads are very similar to those in triads. The two lowest excitations in triads correspond to CT states at ~ 1.7 eV (cf. ~ 1.5 eV in THF in experiment).[3]

C_{60} -BDF- C_{60} dumbbell triads **1-3** ($R = n$ -hexyl; $R' = n$ -octyl)
 $R = R' =$ methyl in calculations

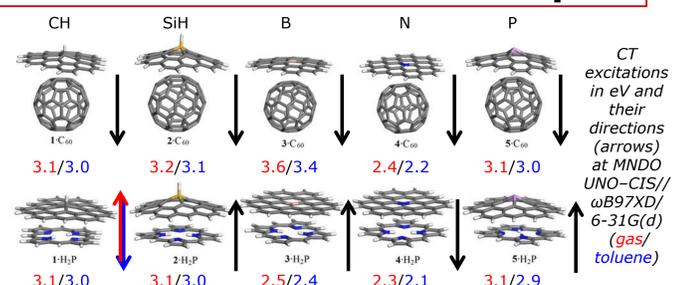
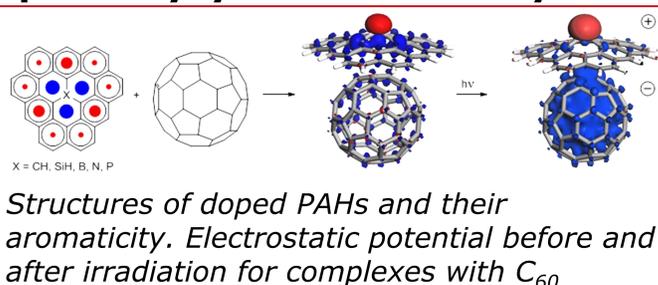


C_{60} -BDF dyads **1d-3d**



3.3 Prediction: Complexes of Doped Polycyclic Aromatic Hydrocarbons with Fullerene and Porphin

MNDO UNO-CIS calculations were used to predict the direction and nature of the charge transfer (CT) states of the complexes of doped PAHs with fullerene and porphin in gas and toluene.[4]



References:

- [1] a) D. M. Guldi, *Chem. Commun.* **2000**, 321-327. b) D. M. Guldi, M. Prato, *Acc. Chem. Res.* **2000**, *33*, 695-703. c) H. Imahori, Y. Sakata, *Adv. Mater.* **1997**, *9*, 537-546. d) H. Imahori, Y. Sakata, *Eur. J. Org. Chem.* **1999**, 2445-2457.
- [2] A. Ciammaichella, P. O. Dral, T. Clark, P. Tagliatesta, M. Sekita, D. M. Guldi, *Chem. Eur. J.* **2012**, *18*, 14008-14016.
- [3] H. Li, C. Schubert, P. O. Dral, R. Costa, A. La Rosa, J. Thüning, S.-X. Liu, C. Yi, S. Filippone, N. Martin, S. Decurtins, T. Clark, D. M. Guldi, *ChemPhysChem* **2013**, accepted, DOI: 10.1002/cphc.201300378.
- [4] P. O. Dral, M. Kivala, T. Clark, *J. Org. Chem.* **2013**, *78*, 1894-1902.
- [5] P. O. Dral, T. Clark, *J. Phys. Chem. A* **2011**, *115*, 11303-11312.



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