Unconventional Donor–Acceptor Molecules for Supramolecular Assembly and Electronics

Bobby G. Sumpter[1], Vincent Meunier[1], Edward F. Valeev[2], Álvaro Vázquez-Mayagoitia[3], Ling Yuan[4], Andrew J. Lampkins[4], Hengfeng Li[4], and Ronald K. Castellano[4]

[1]*Computer Science and Mathematics Division and Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831*; [2]*Dept. of Chemistry, Virginia Tech, Blacksburg, VA 24061*; [3]*Universidad Autónoma Metropolitana Iztapalapa, Dept. de Química, San Rafael Atlixco 186, Col Vicentina, Iztaplapa, Mexico City, DF 09340, México*; [4]*Dept. of Chemistry, University of Florida, P.O. Box 117200, Gainesville, FL 32611*

Proposal Title

Through-Bond Interactions in Nanoscale Self-Assembly (CNMS2004-016) and *Theory-Guided Design of Supramolecular Wires for Optoelectronic Applications* (CNMS2007-029)

Research Achievement

Nanoscale self-assembly of donor-σ-acceptor molecules: Self-assembly lies central to the implementation of a bottom-up approach to design functional organic materials and represents a promising strategy to control bulk electronic and optical properties.[1] Over the past several years, researchers at the University of Florida and Center for Nanophase Materials Sciences (CNMS) at ORNL have shown, through a joint experimental and theoretical study, how the self-assembly of rather "unconventional" donor–acceptor molecules may lead to their broad application in materials science, supramolecular chemistry, and organic electronics.

Molecules containing a donor and acceptor group separated by an insulating spacer (donor-σ-acceptor molecules) have been largely unexplored with respect to their self-assembly and supramolecular electronic properties, despite early enthusiasm.[2] Demonstrated in 2005 was that 1-aza-adamantanetriones (AATs) **1** (Fig. 1a), one class of donor-σ-acceptor molecules, could be designed to rapidly self-assemble in organic solution to form gels and homogeneous fibers (Fig. 1b), and that this macromolecular behavior responded dramatically to chemical modifications of the monomers.[3,4] What has emerged since, through extensive first principles calculations, is a detailed description of the AATs at the monomer, dimer, and multimer levels and a new approach to one-dimensional supramolecular wires based on the systems that have easily tunable electronic and physical properties.[a–c]

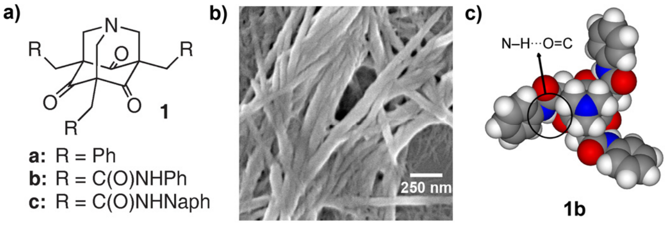

Fig. 1

Both many body perturbation theory (MBPT) and density functional theory (DFT) calculations have identified a propeller-shaped conformation of the AATs **1** as the lowest energy form, additionally stabilized for amide derivatives (e.g., **1b** and **1c**) by weak intramolecular hydrogen bonds (Fig. 1c).[a,b] These gas-phase features are in excellent agreement with experimental data. Theory further shows the proclivity of AATs of this shape to organize into head-to-tail stacked arrays in the gas phase (shown in Fig. 2a for **1a**), a process driven by dipolar and dispersion forces.[a,b] That aromatic stacking interactions are important is shown through the more robust solution-phase self-assembly behavior of naphthyl derivative **1c** versus phenyl derivative **1b**, an observation that agrees well with predicted dimer binding energies (Table 1).[5]

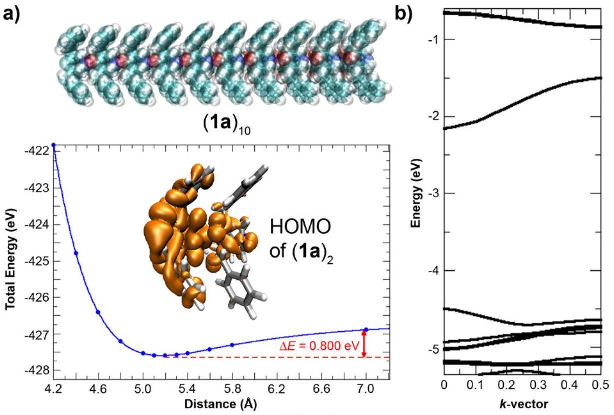

Fig. 2

The simulated X-ray diffraction (XRD) pattern obtained from the optimized supramolecular structure for **1a** also compares favorably to the experimentally-measured XRD spectrum of **1a** as a powder.[a]

Emergent electronic structure and a new class of supramolecular wires: Upon self-assembly of the AATs into 1-D periodic arrays the frontier molecular orbitals are delocalized, spanning the entire system, through the saturated tricyclic cores of the monomers (Fig. 2).[b] The nature of the dispersion is shown by the frontier molecular orbitals of the dimer of **1a** (HOMO shown in Fig. 2a inset) and the electronic band structure for the (**1a**)$_{10}$ assembly (Fig. 2b); the latter can be tuned from the insulating regime to the semiconducting regime by suitable chemical functionalization of the core (Table 1). For example, the supramolecular bandgap spans from 2.3 eV for **1a** (Fig. 2) to 1.5 eV for the triamides AAT **1b** and **1c**.

Table 1. Calculated properties of dimers (assemblies) of **1a–c**.

parameter	(**1a**)$_2$	(**1b**)$_2$	(**1c**)$_2$
binding *E* (eV)	0.40	0.35	0.83
intercore distance (Å)	5.1	5.5	4.9
LUMO–LUMO transfer integral (eV)	0.25	0.16	0.40
E_{gap}[a] (eV)	2.3	1.5	1.5[b]

[a] From plane-wave pseudopotential calculations. [b] This system also exhibits an indirect bandgap of 0.99 eV.

Future Work

We have shown how tunable through-bond donor–acceptor interactions, shape, and aromatic interactions can direct the self-assembly of donor-σ-acceptor molecules in solution and the gas phase. Rigorous theoretical characterization has revealed a supramolecular electronic structure and a conceptual framework for achieving charge transport characteristics from such systems that differ from traditional π-conjugated materials. In future work we will pursue a) strategies to enhance the AAT core-to-core interactions in solution, b) derivatives that show useful macromolecular phases, and c) the design of new synthetic architectures that can exploit through-bond donor–acceptor interactions in the context of supramolecular assembly and novel electronic structure.

References

1) Schenning, A.; Meijer, E. W. *Chem. Commun.* **2005**, 3245–3258.
2) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277–283.
3) Li, H.; Homan, E. A.; Lampkins, A. J.; Ghiviriga, I.; Castellano, R. K. *Org. Lett.* **2005**, *7*, 443–446.
4) Lampkins, A. J.; Abdul-Rahim, O.; Li, H.; Castellano, R. K. *Org. Lett.* **2005**, *7*, 4471–4474.
5) Sumpter, B. G.; Meunier, V.; Yuan, L.; Castellano, R. K., manuscript in preparation.

Publications

a) Sumpter, B. G.; Meunier, V.; Vázquez-Mayagoitia, Á.; Castellano, R. K. “Investigation of the Nanoscale Self-Assembly of Donor-σ-Acceptor Molecules” *Int. J. Quantum Chem.* **2007**, 107, 2233–2242.
b) Sumpter, B. G.; Meunier, V.; Valeev, E. F.; Lampkins, A. J.; Li, H.; Castellano, R. K. “A New Class of Supramolecular Wires” *J. Phys. Chem. C.* **2007**, 111, 18912–18916.
c) Yuan, L.; Sumpter, B. G.; Abboud, K. A.; Castellano, R. K. “Links Between Through-Bond Interactions and Assembly Structure in Simple Piperidones”, *New J. Chem.* **2008**, 32, 1924–1934 (identified as a “hot article”).