


REVIEW



Electron-poor arylenediimides

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Arylenediimides are inherently electron deficient and provide enormous opportunities to conjugate electron withdrawing substituents in different regions of the π -scaffold. This review article highlights the gradual emergence of diverse molecular design principles to realize exceptionally electron deficient arylenediimide molecules. Interestingly, non-conventional electron withdrawing substituents allow the realization of some of the strongest electron acceptors known from this class of molecules. Thus, an enthralling and exceptionally close race to garner the top position within the electron deficient molecules unfolds, which has immense implications with regard to stability and potential applications.

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Introduction

Organic redox-active π -conjugated molecules with strong electron-accepting properties can be important building blocks to cater to the global demand for new generation of renewable energy sources.¹ In this context, there has been a persistent endeavour to develop efficient organic n-type semiconductors to realize large-area, flexible electronics and stable optoelectronic devices, for example, organic field-effect transistors (OFETs), organic photovoltaics (OPVs) and organic light-emitting diodes (OLEDs).² Although there have been significant advances

towards enhancing the charge mobility of n/p-type semiconductors, a comprehensive understanding of the fundamental relationship between the molecular structure and its electronic and physicochemical properties would be required for replacing the currently utilized metal and silicon-based electronic components in the existing devices.³ To this end, a lot of work has been done on multi-centred hole-transporting materials and p-type semiconductors have seen a significant improvement in performance over the last few years.⁴ However, the development of n-type materials with high mobility and stability under ambient conditions remains a major challenge for the realization of complementary circuits. This is because the synthesis of molecules with very low-lying LUMO energy levels results in instability and high reactivity under ambient conditions.⁵

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highly electron rich molecules, preparation of stable radicals/radical ions, and their opto-electronic and magnetic properties. He is also interested in the investigation of intramolecular noncovalent interactions and their applications in the stabilization of reactive systems.



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and multistate electron reservoir systems for their application in advanced energy storage systems. She is also involved in the studies of counter anion dependent ionic organic proton conducting materials for application in fuel cells and rigid rectangular molecular boxes with supramolecular and material aspects.

de Leeuw and co-workers have explained the instability of n-type organic molecules to ambient conditions on the basis of kinetic barriers for the reaction of the charge carrying electron with common reactive species like H_2O and O_2 .^{6a} On the basis of their solution-phase redox potentials, it was proposed that to possess water stability, molecules should have reduction potential more positive than -0.658 V , while for oxygen stability, first reduction potential should be more positive than $+0.571\text{ V}$ vs. the saturated calomel electrode (SCE). However, with some apt molecular designing ambient-stable n-type semiconductor devices have been fabricated with a LUMO level of -4.0 eV , which is at significantly higher potential than that estimated by de Leeuw.^{6b-e} On the other hand, the significant challenges in the synthesis and isolation of molecules with the LUMO level lower than -4.5 eV have been confirmed by the groups of Diederich and Chi *et al.*^{7,25} In certain cases, molecules having such low-lying LUMO energy levels are even reactive to the glass surface rendering their isolation extremely difficult.

Traditionally, perfluoro groups, halogen atoms, cyanide and nitro groups have been utilized as electron withdrawing substituents and poly-aromatic hydrocarbons substituted with such groups showed enhanced electron accepting properties, and strong charge mobility.⁸

Among the inherently electron deficient π -acceptors, arylenediimide based π -scaffolds have been widely investigated as semiconductors, radical ion-based sensor probes, charge transporting materials, solar cells, in energy storage and in catalysis of reactions.^{9,10} Out of the arylenediimides, naphthalenediimides (NDI)¹¹ and perylenediimides (PDI)¹² have been established as promising electronic materials because of their

large electron deficient π -surfaces and ability to form self-assembled structures. It is to be noted that these compounds are also termed naphthalene bisimides (NBIs) and perylene bisimides (PBIs), which is the short form for naphthalene and perylene bis(dicarboximide). The energy of the frontier molecular orbital levels (HOMO and LUMO) of these diimides can be easily tuned *via* diverse chemical functionalization at the core- and axial-positions.¹³ The introduction of electron withdrawing groups at the core-position significantly lowers down the LUMO level, which not only enhance the stability in the presence of ambient impurities H_2O and O_2 but also improve the charge injection at the electrode.¹⁴

The aim of this review article is to highlight the gradual emergence of diverse molecular design principles that have led to the realization of exceptionally strong arylenediimide-based electron acceptors. A host of new electron withdrawing substituents have been conjugated with the arylenediimides, which has significantly expanded the tool-box available to synthetic chemists enabling the engineering of molecules with remarkably low-lying LUMO levels as well as stability. As a result, a fierce race to attain the lowest LUMO is currently on, and is fascinating to see how it unfolds through this review article. We also consider some recent versatile applications that emanate from the electron deficiency of arylenediimides.

Naphthalenediimides (NDIs)

The NDI π -scaffold is one of the most extensively studied organic electron deficient system with excellent thermal, light



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Pritam Mukhopadhyay

Pritam Mukhopadhyay obtained his B.Sc and M.Sc degrees from Calcutta University, India. He obtained his Ph.D. from IIT Kanpur, India under the guidance of Prof. P. K. Bharadwaj. He then joined the group of Prof. L. Isaacs at the University of Maryland, College Park, USA as a post-doctoral fellow, where he worked on the synthesis and studies of complex self-sorting systems. Later, he worked with Prof. S. Shinkai at the Kyushu

University, Japan as a JSPS fellow. He then joined the School of Physical Sciences, Jawaharlal Nehru University, New Delhi, India, where he is currently an Associate Professor. His group's research interests involve the synthesis and stabilization of organic radical ions, stabilization of highly electron-deficient and electron-rich systems and applications related to electron transfer reactions. The group is also interested in the design and synthesis of new supramolecular materials, e.g. ferroelectric, piezoelectric, NLO-active and magnetic materials.