

Molecules with Exceptionally Small HOMO–LUMO Gaps**

Dmitrii F. Perepichka* and Martin R. Bryce*

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The engineering of small band gaps in π -conjugated heteroaromatic polymers by chemical manipulation has been widely studied for the last 20 years in the search for materials with tailored optoelectronic properties,^[1] such as intrinsic conductivity, infrared electrochromic displays, and charge-storage capability.^[2] The two most successful approaches are 1) tuning bond-length alternation in the π -system by stabilizing quinonoid character (polyisothionaphthalene (PITN) is the classical example^[3]) and 2) alternating heteroaromatic donor and acceptor units.^[1,4] Most of these materials are modified thiophene derivatives, obtained by chemical or electrochemical polymerization. A band gap of 0.5 eV and smaller, usually determined by the on-set of absorption or the difference in oxidation/reduction on-set potentials, has been reported.^[1] However, if the absorption or redox peak maxima are considered, rather

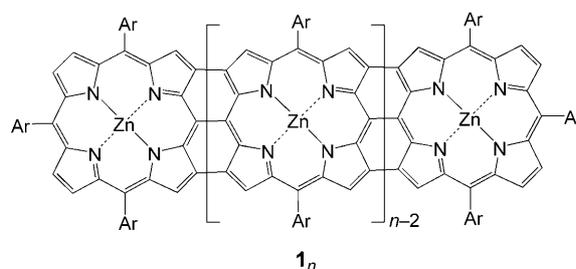
than ill-defined on-set values, there are very few examples of polymers with electrochemical or optical gaps smaller than 1.0 eV.^[4]

The attraction of molecular systems is their precise chemical structure and better defined frontier-orbital levels that are unperturbed by supramolecular band formation, which makes them ideal models for basic studies of electron-transfer phenomena as well as potential objects for molecular electronics.^[5] There are two established approaches to decreasing the HOMO–LUMO gap (HLG) in a molecule: one is to extend the conjugation, the other is to covalently link electron-donor (high HOMO) and electron-acceptor (low LUMO) fragments. However, the design and synthesis of very-small-HLG systems (<0.5 eV) present considerable challenges.

Early predictions that large polyacenes (that is, conjugated polyaromatic hydrocarbons (PAHs) with linearly fused benzene rings) may behave as one-dimensional conductors with a zero band gap are contradicted by the most recent calculations.^[6] The HOMO–LUMO gap of hexacene determined from both the UV/Vis spectra and density functional theory (DFT) calculations is approximately 1.8 eV; higher homologues are calculated to have an open-shell singlet ground state.^[6] Also, the aromatic stabilization in graphenetype PAHs is predicted to keep the HLG above 1 eV even for large (over 200 carbon atoms) graphene molecules,^[7] although the band formation in the solid

state reduces the (band) gap for PAH $C_{222}H_{42}$ to about 0.6 eV (determined by absorption on-set).^[8]

It was, however, demonstrated that conjugation over the planar π -electron platform in the triply linked, fused-porphyrin ribbons **1** results in exceptionally small HLGs which are mani-



fest in remarkably red-shifted absorption spectra.^[9] The longest fused array, a dodecamer **1**₁₂ of approximately 10-nm length, has the longest wave-length absorption band at $\lambda_{\max} \approx 2900$ nm (3500 cm^{-1} ; Figure 1), which corresponds to an electron transition energy of as low as 0.45 eV to < -0.25 V versus Ag/AgClO_4 . The one-electron-oxidation potential decreases progressively with an increase in the number of porphyrin units. Unfortunately, the electrochemical reduction of these molecules, which is expected to occur at easily accessible potentials, has not been investigated. Most unexpectedly, in spite of such low oxidation potentials the molecules are claimed to be air-stable, and prospective applications in near-IR and IR sensors, and conducting molecular wires, were suggested.

Another way to attain a small HLG is to couple electron-donor (high HOMO) and electron-acceptor (low LU-

[*] Prof. D. F. Perepichka
INRS-ÉMT
Université du Québec
Varennes, J3X1S2 (Canada)
Fax: (+1) 450-929-8102
E-mail: perepichka@emt.inrs.ca

and
Institute of Physical Organic and Coal
Chemistry
National Academy of Sciences of Ukraine
Donetsk 83114 (Ukraine)

Prof. M. R. Bryce
Department of Chemistry
University of Durham
Durham, DH1 3LE (UK)
Fax: (+44) 191-374-3848
E-mail: m.r.bryce@durham.ac.uk

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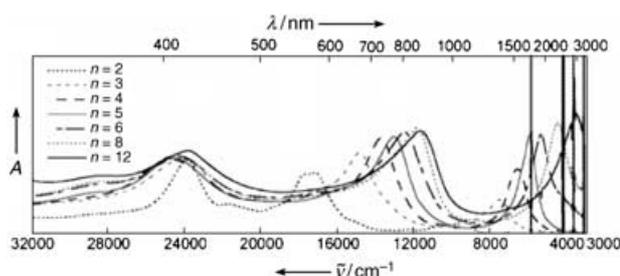
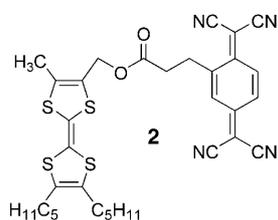


Figure 1. Electronic absorption spectra of porphyrin ribbons **1** with different numbers of units ($n = 2-12$).^[9b]

MO) fragments in a single molecule. A significant difference between the previously described conjugated systems (which generally fit within a broader concept of small-band-gap materials) and the covalent donor–acceptor molecules is that different location of the HOMO and LUMO orbitals hinders the electron transition between them. Thus, a donor–acceptor molecule with zero HLG is not expected to show metallic (non-activated) conductivity, although this limited HOMO–LUMO interaction may be attractive for other applications. The first interest in such systems was presented in a famous proposal by Aviram and Ratner where a hypothetical TTF- σ -TCNQ molecule (TTF = tetrathiafulvalene; TCNQ = tetracyanoquinodimethane) with an HLG of 0.3 eV was predicted to act as a unimolecular rectifier.^[10] Since then, this type of molecule has been a target for many research groups, although the challenge of preparing such a highly electrochemically amphoteric molecule was only overcome recently. Thus, the reaction of a TTF lithium alcoholate and a TCNQ acid chloride at -100°C favored covalent coupling (i.e. ester formation) over electron-transfer processes, and the TTF–TCNQ diad **2** was prepared in



analytically pure form.^[11,12] Two reversible oxidations and two reversible reductions in cyclic voltammetry (CV) experiments are characteristic of the TTF and TCNQ moieties, respectively,

and the difference between the $E_{1\text{ox}}^0$ and $E_{1\text{red}}^0$ values suggests an HLG of only 0.17 eV (Figure 2a). Such a low barrier allowed the first observation of a ther-

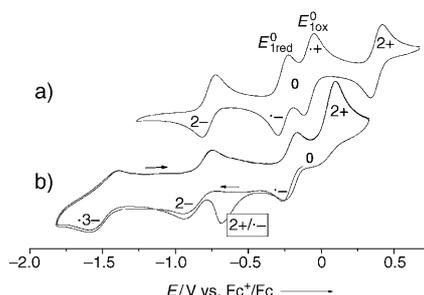
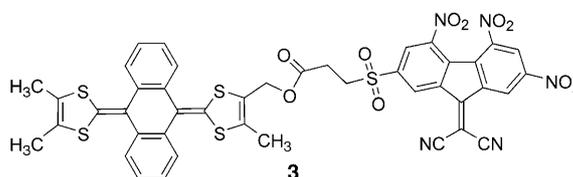


Figure 2. a) Amphoteric multiredox behavior of **2** in CV experiments; b) generation of a charge separated state $2+/-$ of **3** in CV experiments at -15°C ; $\text{Fc} = [(\eta\text{-C}_5\text{H}_5)_2\text{Fe}]$.

mo-excited electron-transfer in an organic molecule. Indeed, the solution ESR signal of **2** increases at higher temperatures (approximately 1% of the molecules are in a biradical form $\text{TTF}^{+\cdot}\text{-}\sigma\text{-TCNQ}^{\cdot-}$ at room temperature).

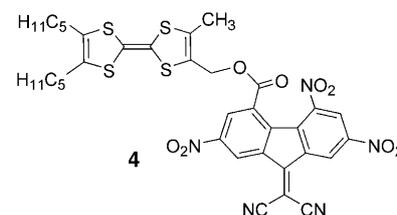
Other novel electron-transfer phenomena are likely to arise in small-HLG molecules. Combining a π -extended TTF donor (TTFAQ) with a polynitrofluorene acceptor affords the diad **3**, in



which the small gap between the oxidation and reduction, combined with quasi-reversibility of the TTFAQ oxidation (that is, re-reduction of TTFAQ^{2+} required a lower potential than the initial

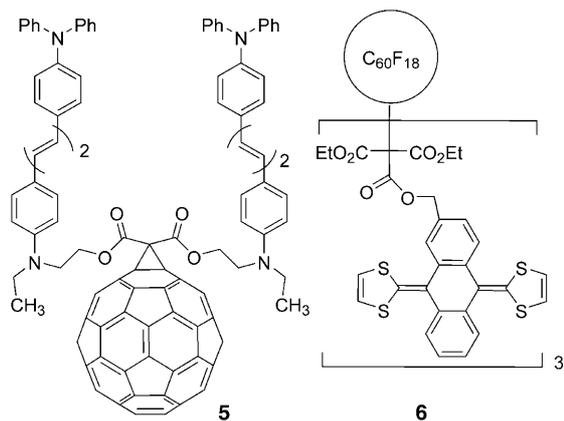
oxidation) result in a remarkable property.^[13] When the potential was initially scanned in the positive region (forming the dication) and then reversed, the reduction peak (arising to formation of the fluorenone radical anion) preceded the re-reduction of the TTFAQ dication to the neutral species (Figure 2b). Consequently, a most unusual charge-separated state of **3**, $\text{D}^{2+}\text{-}\sigma\text{-A}^{\cdot-}$, was formed (D = donor, A = acceptor).^[13]

A molecular electronics application of TTF-based donor–acceptor diads with small HLG was recently demonstrated for the TTF–fluorene diad **4** (HLG 0.3 eV). When **4** was immobilized



in Langmuir–Blodgett monolayers between n-doped silicon and titanium or gold and thiol-protected mercury electrode pairs, asymmetric rectifying electrical characteristics were observed.^[14] The molecular origin of the current–voltage (I – V) asymmetry was demonstrated by the alignment dependence of the rectification, which changed direction for monolayers transferred onto the electrode in opposite orientations (X and Z deposition).

Buckminsterfullerene is another prominent example of an electron-acceptor molecule, although its reduction potential (-1.06 V versus Fc/Fc^+) is too low to attain a gap of less than around 1 eV in diads with air-stable electron donors (donors with an oxidation potential less than approximately -0.1 ... -0.2 V vs. Fc/Fc^+ are usually doped when exposed to air). Numerous donor– C_{60} diads with gaps of 1–2 eV have been synthesized and used for fundamental studies of photoinduced electron-transfer processes, and as photovoltaic materials.^[12,15] A fullerene–arylamine based D–A compound **5** with an electrochemical gap of about 1 eV was recently exploited as a



unimolecular rectifier.^[16] The junctions prepared with Langmuir–Schaefer (horizontal transfer) monolayers sandwiched between two gold electrodes were found to be very robust up to ± 5 V and reveal a rectification of approximately 16:1 at high biases (with a symmetric I - V behavior at lower voltage). Interestingly, the rectification direction is the same as found in other D- σ -A molecules (**4**), but opposite to that revealed by D- π -A molecules.

The HLG in fullerene systems can, however, be pushed below 1 eV by employing fluorinated C_{60} derivatives which are much stronger acceptors. Thus, the cyclic voltammetry of TTFAQ- $C_{60}F_{18}$ compound **6** (Figure 3) demonstrates high electrochemical am-

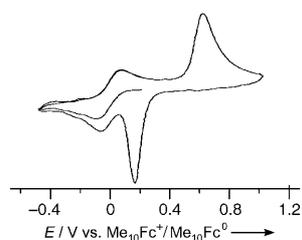


Figure 3. The cyclic voltammogram of compound **6**. Redrawn from ref. [17]; $Me_{10}Fc = [(1-C_5Me_5)_2Fe]$.

photericity, with a reversible reduction of the fullerene moiety and a quasi-reversible two-electron oxidation of the TTFAQ moiety, with the gap between the oxidation and reduction peaks of the two-electron event being nearly 0.5 eV.^[17] Time-resolved fluorescence studies suggested formation of a charge-separated state ($(TTFAQ^+) \cdot \sigma$ -

$(C_{60}F_{18}^-)$) whose low energy resulted in a very long life-time of around 1 μ s.

An approach which combines both the extended conjugation and the donor–acceptor concepts is exemplified by TTF–dithiolato metal complexes **7** (Figure 4). Based on electronic-absorption spectral bands that are shifted into the IR region, the neutral nickel complexes **7** are remarkably small-band-gap molecular solids.^[18] The

first electronic transition of dialkyl–TTF complexes **7A** and **7B** in the solid state occurs in the mid-IR region at $h\nu_{max} = 0.27$ eV and a nearly zero band gap can be assumed based on the absorption on-set (Figure 4). Performing band-structure calculations and fitting with the experimental spectral data,

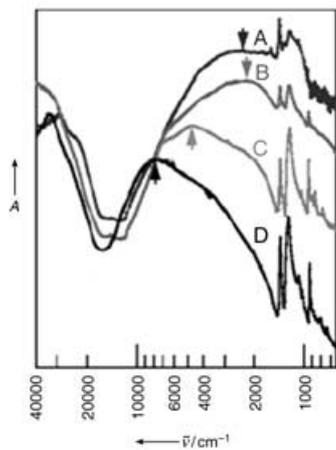
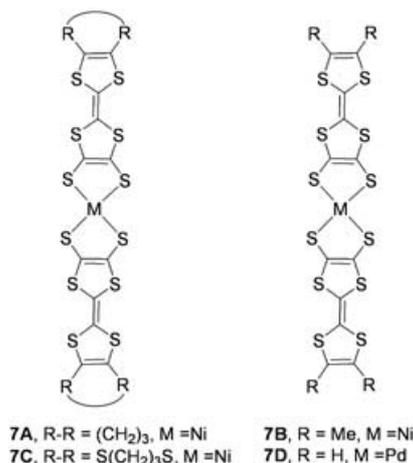


Figure 4. Electronic absorption spectra of TTF–M complexes **7A–D**.^[18]

a molecular HLG of 0.14 ± 0.06 eV was predicted. Although the accuracy of the extended-Hückel calculations might be disputable, a D–A complexation in the solid state may result in increased optical gap versus the molecular HLG. Furthermore, electrochemical data for the anion of **7C** in which the difference between the first and the second oxidation potentials (0.3 V)^[19] should correspond to the HLG of the neutral complexes, is also lower than the optical gap ($h\nu_{max}$) of the solid complex **7C** (0.58 eV).^[18]

In contrast to small-band-gap polymers, where intrinsic conductivity was envisaged but has never been observed, the TTF–metal complexes with exceptionally small HLGs are single-component molecular metals with high conductivity down to 0.6 K ($\sigma_{rt} = 400$ Scm^{-1} for **7A**, 350 Scm^{-1} for **7B**).^[20] Notably, the higher HLG for the complexes **7C** and **7D** (optical gaps of 0.58 and 0.97 eV, respectively) results in semiconducting properties ($\sigma_{rt} = 7$ Scm^{-1} and 0.5 Scm^{-1} , respectively).^[18]

Thus, in the recent years molecules with exceptionally small (< 0.5 eV) HOMO–LUMO gaps have become synthetically achievable targets. A variety of unusual optoelectronic properties and electron-transfer phenomena have already been demonstrated for these compounds, making them as very desirable targets for further physical studies and electronics applications.

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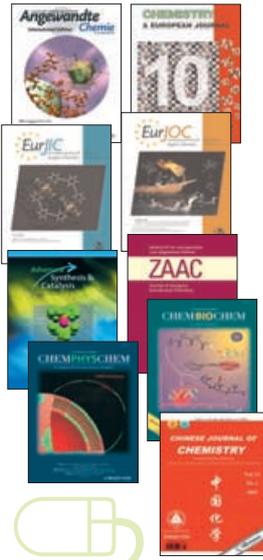
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