

Organic-Based Electronics à la Carte

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Introduction

Organic-based devices, thin film transistors, and light-emitting diodes have been recently proposed in which the thin semiconducting layer is made from a conjugated material, e.g., an oligothiophene or poly(phenylenevinylene), respectively.^{1,2} These results raised a great interest, because of both the fundamental understanding of the semiconducting properties of organic materials and also the large potential presented by this new generation of devices. Organic semiconductors, which have been brought close to the application market, offer the interest of low-temperature processing, flexibility, low cost, and large-area devices. This field is called “polymer electronics”.¹

This potential also raised great interest in the chemical community for the design of new classes of conjugated materials with enhanced semiconducting properties.

What are the structural parameters controlling the electrooptical properties of conjugated materials which could allow the à priori tuning of device characteristics?

A critical analysis of literature data should allow discussion of the macroscopic semiconducting properties of a material in terms of the molecular properties of the elemental bricks, i.e., the molecules which constitute this material. In this regard, we will report in this Account on some relationships among (i) the intimate chemical structure of the molecular units involved in the construction of the material, (ii) the spatial organization of these (macro)molecular assemblies, i.e., how these elemental bricks are assembled in the macroscopic material, and finally (iii) the electric and electrooptical properties of these materials, which define their relevance for building organic-based devices. Such knowledge should provide a research strategy for the rational tuning of material properties.

The tentative rationalization of the electrooptical properties of a conjugated material can be formulated in terms of the fate of a photonic or electric excitation. When considered as a whole, such an energized system can

evolve either toward the production of a charge or toward the release of a photon, in addition to losses through trapping of charges or nonradiative decay, which will not be further considered. These two alternative routes encompass the characteristics of the main devices which can be built, i.e., (i) thin film transistors, only based on charge transport, (ii) light-emitting diodes, involving conversion of charged states into excitonic states followed by their radiative decay, (iii) photoconductors and photovoltaic cells, requiring conversion of photons into charges, charge transport, and collection, and (iv) optically pumped light sources, requiring light absorption and emission, as in lasers. Evidently, (i) and (iii) are reverse processes when compared to (ii) and (iv), which raises the important issue that a material cannot be at the same time efficient for producing charge and also for delivering photons. A tradeoff should thus exist between the competitive routes for an excitation, either toward charges or toward photons.

Structural Organization and Electric Properties of Conjugated Materials

As evidenced by the first work on polyacetylene, effective conjugation length is key for extended delocalization of charges in conjugated polymers, although strong electron–phonon coupling in such a 1-dimensional semiconductor leads to “self-localization” of charged excitations, expressed by the polaronic effect. Although conductivity of oriented and defect-free polyacetylene has been shown to reach that of metals,³ most other conjugated polymers possess a high content of conjugation defects and impurities originating from their uncontrolled polymerization, and charge transport in these materials is mainly limited by the low efficiency of interchain charge hopping. Conductivity is however not the most adequate parameter for rationalizing the charge transport properties of organic conjugated materials, as it directly depends on the carrier concentration, which is difficult to assess from their doping level. Carrier mobility on the other hand is a very relevant parameter, as it directly expresses the velocity of charges under an applied electric field. First experiments devoted to field-effect transistors based on neutral semiconducting polymers, polyacetylene, polypyrrole, or polythiophene have evidenced an extremely low mobility, on the order of $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which has been attributed to the high structural disorder of these polymers.

On the other hand, short conjugated oligomers, e.g., oligothiophenes,⁴ have been subsequently developed, in which the conjugation length is much shorter than the mean conjugation length in the parent polymer, e.g., polythiophene, but the monodisperse conjugation length allows these molecules to be highly organized when assembled into a film. Control of substrate temperature and rate of deposition, or thermal annealing of a sexithiophene film, allow the degree of molecular organization to be monitored, as shown by X-ray characterization, from a mostly amorphous to a polycrystalline state, with further control of the crystallite size.⁵ Resolution of

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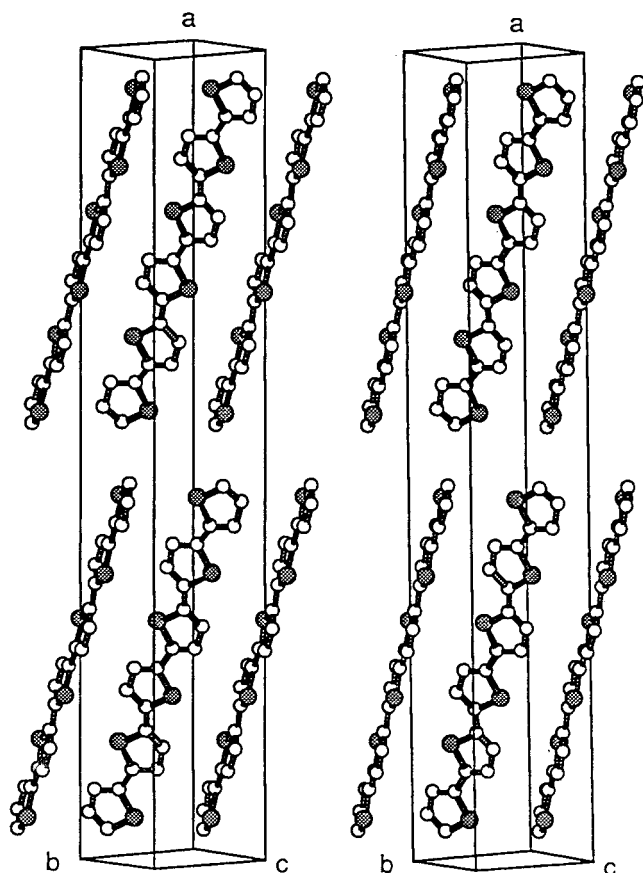


FIGURE 1. Stereoscopic view of the unit cell of the sexithiophene single crystal.

the single-crystal structure of sexithiophene,⁶ 6T, Figure 1, shows that the molecules are rigorously planar, all parallel to each other and organized in H-type aggregates as often encountered in molecular materials, e.g., oligophenylenes. The observed dense herringbone packing is common to many planar molecules, and the short interatomic distances predict strong intermolecular coupling in these lamellar molecular semiconductors with quasi-2-dimensional structure.

Charge transport in these oligomers involves successive intermolecular charge hopping steps, following a mechanism already described in charge-transfer complexes TTF-TCNQ,⁷ which bears a high degree of directionality along the stacking axis of the planar conjugated molecules. Although the macroscopic charge transport in short oligothiophenes requires a much higher frequency of charge hopping between conjugated molecules than in the case of polythiophenes, the field-effect mobility of sexithiophene increased dramatically, from about 10^{-5} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ in a fully amorphous film of polythiophene to 2×10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ in a partially organized film of 6T, and up to 10^{-1} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ in a single crystal of 6T.^{5,8,9} The anisotropy of conductivity also strictly follows this trend, passing from fully isotropic in amorphous films to a ratio of 30 in favor of the stacking axis of the conjugated molecules in the case of the highly oriented 6T film.

This relationship between structural order and carrier mobility, later confirmed in the case of pentacene and

more recently in the case of stereoregularly alkyl-substituted polythiophene, shows that although intermolecular charge hopping is of low efficiency, it can be overcompensated by an almost perfect structural organization. The high performances obtained with oligomer-based field-effect transistors clearly evidence that long-range ordering and a high degree of molecular close packing are keys for charge transport in conjugated materials.

Structural Organization and Optical Properties of Conjugated Materials

The optical properties of conjugated materials are of considerable interest, particularly for the understanding of the subtle interplay between material organization and the energy diagram describing their ground and excited states, and also for the development of efficient electrooptical devices. In this regard, oligomers also appear to be interesting model compounds, and the discussion of their solid-state characteristics in terms of molecular properties should bring the essential information for the ultimate goal of tuning molecular structure for given macroscopic electrooptical properties.

When dissolved in solution, 6T molecules show free rotation along the C-C bond between thiophene units, which leads to a large unstructured absorption band located at about 2.85 eV (435 nm), with a molecular absorption coefficient of $5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The high quantum yield of fluorescence in solution, 0.4, confirms that the observed electronic transition between the ground 1^1A_g and the lowest 1^1B_u excited states is fully allowed. When rigidified as isolated molecules in various matrixes,¹⁰ 6T shows highly structured luminescence and excitation spectra, with a vibronic progression of 0.18 eV, corresponding to a C=C vibration frequency observed in Raman spectroscopy. This feature indicates that the rigidified conjugated molecules adopt a mostly planar structure, in both their ground and excited states. The high photoluminescence yield, about 0.4, indicates that the 0-0 transition is fully allowed, with a lowest 1^1B_u excited state. These results confirm that neutral excitations of isolated 6T molecules lead to the formation of excited states in which excitation energy is strongly localized, described as Frenkel excitons.

A dramatic change of optical properties occurs on going to the solid state. The absorption spectrum, Figure 2, shows (i) an onset of a weak absorption at 2.3 eV, (ii) an important shift of the absorption maximum toward higher energies, $E_{\text{max}} = 3.5$ eV, (iii) a peculiar shape of the absorption band, with a slow increase from the lower energy side, and a steep decrease at higher energies,¹¹ and (iv) a large dichroic ratio when using polarized light.

These results can be understood in the frame of the Frenkel molecular exciton theory which predicts the formation of exciton levels in molecular crystals.¹¹ The existence of two independent sublattices of fully parallel molecules, Figure 1, gives rise to the formation of an excitonic band, associated with Davydov splitting. Al-

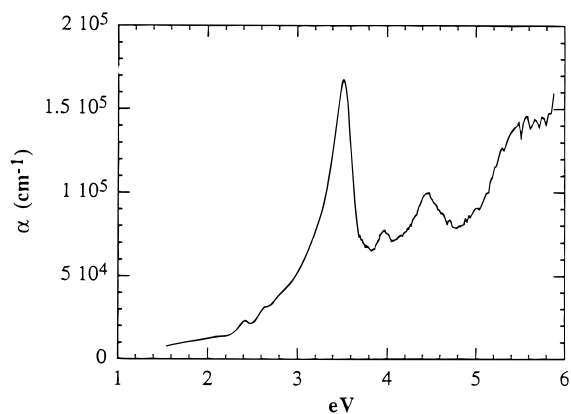


FIGURE 2. Absorption spectrum of a thin film of conjugated sexithiophene.

though there is a discrepancy in the literature on the calculated energy bandwidth, from $E = 1$ eV to $E = 0.3$ eV,^{11,12} it is agreed that all the oscillator strength is reported on the upper 1^1Bu level of this band, in agreement with the very intense absorption, Figure 2. Another important consequence of this band splitting concerns the oscillator strength associated with the lowest excited level of this excitonic band, i.e., an 1Au (or 2Ag) level, which becomes forbidden or at most very weakly allowed.¹² Thus, optical transitions between the ground state and the lowest excited state are very weak, both in absorption and in emission, in agreement with (i) the very low absorption coefficient of the $0-0$ transition at the onset of absorption, about 400 cm^{-1} at 2.3 eV , and (ii) the collapse of the quantum yield of photoluminescence, on the order of 10^{-3} . This behavior appears to be very general for planar conjugated oligomers forming H-type aggregates, in which intense absorption is followed by an ultrafast relaxation of upper excited states to the lowest excited state, from which however no fluorescence can be recovered. On the other hand, the luminescent properties of conjugated oligomers can be restored by a chemical modification of these oligomers, through the grafting of bulky substituents on their terminal α and ω or lateral β position, which leads to an increase in the intermolecular distances. These latter semiconductors retain most of their molecular luminescent properties when assembled into thin films, due to the vanishing of the intermolecular interactions, as is the case of oligomers dispersed in matrixes, or of amorphous conjugated polymers.¹³ In conclusion, whereas strong intermolecular interactions developed in thin films of conjugated oligomers are very favorable for charge transport, they dramatically affect their optical properties. Davydov splitting of the excited-state levels condemns the lowest excited state, from which energy is consumed in nonradiative decays. On the contrary, amorphous conjugated polymers and substituted oligomers, which behave almost like free molecules in the solid state, retain most of their photoluminescent properties, making these materials attractive for luminescent devices.

Structural Organization and Electrooptical Properties of Conjugated Materials

If photon excitation of conjugated oligomers cannot be recovered through photoluminescence, what is the fate of an excitation? Various escape routes, apart from relaxing to the forbidden lowest excited state, exist for upper excited states which have already been identified by the use of optoelectronic techniques.

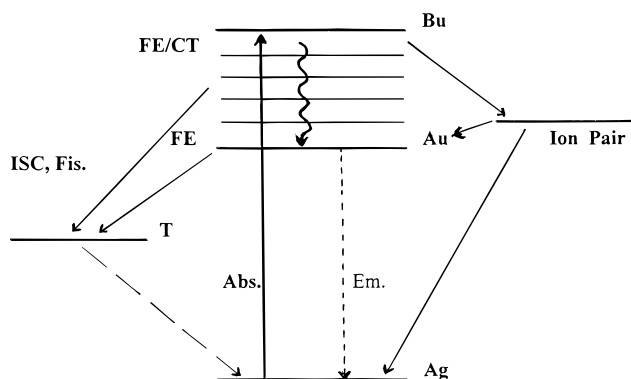
At an onset of 2.3 eV , neutral photoexcitations lead to excited states in which the energy is strongly localized as an electron-hole pair on the same molecule, i.e., *Frenkel excitons*. However, strong overlap of molecular orbitals between neighboring molecules, associated with the dense packing of 6T molecules in the solid state, allows *charge-transfer (CT) states*, in which the electron and hole pair are dissociated on two adjacent molecules, to mix with Frenkel states. The probability of formation of such CT states increases rapidly with excitation energy, as experimentally evidenced by electroabsorption studies beyond the excitation energy threshold of 2.7 eV .¹⁴ Furthermore, charge transfer appears highly anisotropic, the oscillator strength being directed preferentially along the long axis of the molecule, which means that the CT state involves two neighboring 6T molecules belonging to two adjacent layers in this 2-D semiconductor. When taking account of the very high intrinsic carrier mobility, it can be expected that these CT states will efficiently lead to a drift of the charges within each layer, and hence into separate *ion pairs*. Thus, efficient routes exist for the dissociation of a electron-hole pair onto two adjacent layers, and a further separation of charges, offering a high yield for photon-to-charge conversion in conjugated oligomers. Photoconduction experiments carried out on thin films of 6T have confirmed the existence of such energy-dependent branching between luminescence and singlet excitation dissociation into charged states,¹⁵ with a quantum efficiency of charge photogeneration of about 1 together with a simultaneous collapse of the fluorescence quantum yield. These results indicate that in 6T films (i) the yield of primary electron-hole pair formation is very high, (ii) the probability of dissociation into a pair of free charge carriers approaches unity, and (iii) the electron-hole geminate recombination is low. More recent measurements on electric field modulated photoluminescence and photoconduction of 6T thin films¹⁶ have confirmed the energy-dependent electric-field-mediated branching between the luminescence and dissociation of the emitting excited states. The results have been interpreted by the occurrence of an Onsager-type dissociation of weakly bound electron-hole pairs created in the primary process, with an efficiency close to 0.9, while the fluorescence efficiency drops. The calculated primary separation distance, $r_0 = 22\text{ \AA}$, is close to the interlayer distance obtained from X-ray characterization of 6T, which confirms that the initial charge-carrier separation occurs between the nearest neighbor molecular layers in the layered structure of the microcrystalline films of 6T. Photoconduction measurements on 6T lead thus to the conclusion that a very

efficient route exists, beyond the energy threshold of 2.7 eV, for excitations to be directed toward the production of charged states, dissociated on adjacent molecular layers in this organic 2-D semiconductor.

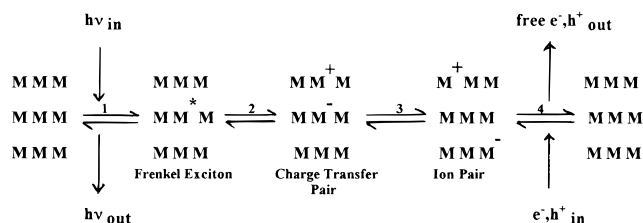
On the other hand, primary excitations in conjugated polymers, e.g., PPV, are essentially neutral, which means that the generation of charges via photoexcitation is a secondary process resulting from the dissociation of an initially neutral excitation possessing excess energy. Dissociation into charged states and photoluminescence are hence competitive processes,¹⁷ and the prevalence of photoluminescence in PPV shown by its very high quantum yield of 0.5 indicates that electron–hole dissociation is an energetically uphill process. The important luminescent properties of PPV have also been associated with the distribution of its excited states, the allowed 1^1Bu excited state lying about 0.5 eV lower than the forbidden 2^1Ag state.¹⁸ Upon low-energy photoexcitation, neutral excitations are initially generated within a manifold of delocalized excited states of segments of the PPV chain possessing different effective conjugation lengths. Relaxation occurs then at the tail of the density of excited states, which emits fluorescence. A tradeoff exists between loss of exciton binding energy and gain in electrostatic energy of the dissociated electron–hole pair, and the relative importance of intra- versus interchain processes depends on intrachain coupling and on topological packing, i.e., the degree of disorder and excited-state energies. Experimentally, the yield of photoconduction under an electric field $E = 10^4 \text{ V cm}^{-1}$, on the order of 10^{-4} ,¹⁷ indicates that the formation of an off-chain electron–hole pair from an on-chain excitation is a largely endothermic process and that, due to large effective conjugation length, it is difficult to overcompensate the expense in coulomb energy by the gain in delocalization energy. In conclusion, PPV, as representative of long conjugated polymers, shows an almost opposite behavior when compared to oligothiophene. This mostly disordered 1-D polymer possesses an allowed lowest excited state, both for absorption and for emission, and the energetics of the emission process of excited states is highly favored over their dissociation into charged states.

Another significant escape route for an excitation in conjugated materials is via the formation of a *triplet state*, 1^3Bu , which is separated from the lowest excited singlet state (generally 1^1Bu) by the singlet–triplet energy splitting $\Delta(S-T)$. This triplet state is dipole forbidden, excluding any significant radiative contribution from this state. However, the contribution of this triplet state is of importance since (i) it is competitive with fluorescence and also since (ii) this long-lived state possesses a large diffusion length, allowing it to be easily captured and ionized by impurities, by the mechanism $\text{T}^* + \text{D} \rightarrow \text{So} + \text{D}^* \rightarrow \text{D}^+ + \text{e}^-$. Triplet states can thus be inferred as very efficient ionizing species, and significantly contributing to the photoinduced generation of free charges in a material. Various routes exist for the conversion of primary excitations to a triplet state: (i) the classical intersystem crossing, ISC, which is promoted by spin–orbit coupling,

Scheme 1. Energy Diagram for Excitations in a Film of Conjugated Oligothiophene, Involving Strong Absorption (Abs) to Frenkel Excitons (FE) and Charge-Transfer Excitons (CT), Low Emission (Em), Relaxation to Ion Pairs, and Intersystem Crossing (ISC) or Fission (Fis) to the Triplet State (T)



Scheme 2. Electron-Optical Pathways in Conjugated Materials Made from Conjugated Molecular Units M



(ii) the fission process from highly excited singlet states,² when the energy of the primary photoexcitation, E_{Sn} , is larger than twice the energy of the triplet state, $\text{Sn} + \text{So} \rightarrow [\text{T}, \text{T}] \rightarrow 2\text{T}$.

In conclusion, steady state as well as transient optical and electrooptical techniques have allowed the mapping of the simplified schematic diagram shown in Scheme 1 which features the main routes followed by an excitation. In the case of oligothiophenes, the extremely low yield of photoluminescence and simultaneous very high yield of photogeneration of charges are a direct consequence of its particular 2-D structural organization, which is also responsible for its highly efficient charge transport properties. On the other hand, conjugated polymers, which are mostly amorphous, show quite opposite properties, i.e., low charge transport, high yield of photoluminescence, and low yield of photogeneration of charges.

Electrooptical Fate of an Excitation in Conjugated Materials

Is it now possible to draw some more general relationships among (i) the intimate chemical structure of the conjugated molecular units, (ii) the structural organization of the (macro)molecular assemblies, and (iii) the electric and electrooptical properties of these materials? We will consider the elemental steps contributing to the fate of an optical or electric excitation in conjugated materials, Scheme 2.

Process 1 corresponds to the one-photon vertical transition to the lowest excited 1^1Bu level, with energy E_1 . This neutral ($\pi-\pi^*$) excitation leads to a Frenkel exciton,

with a strongly localized electron–hole pair.²⁰ Excitations to upper excited states also occur, which relax very rapidly to the lowest excited state or if sufficient energy is available undergo other pathways to charged states or to the triplet state. For clarity, other optical transitions, e.g., to the triplet state, have not been included. Process 1 is reversible, and luminescence can be observed depending on the population of the lowest excited state and on the allowedness of the radiative transition to the ground state.

Process 2 corresponds to the dissociation of a bound electron–hole pair onto two adjacent molecules, or conjugated segments, leading to a charge-transfer pair.²¹ The energy difference E_2 involves Coulomb interactions as well as dispersion forces, and the CT level is generally above that of 1^1Bu since charge separation costs energy.

Process 3 is associated with adjacent nonoverlapping ions, and represents the net attraction E_3 between the electron and hole. It involves electrostatic interactions, together with induced dipoles at other molecules and dipole–dipole interactions. The relative energies of the 1^1Bu level and that of ion pairs are crucial in controlling the electrooptical properties of organic semiconductors.

Process 4 represents energies for ion pair relaxation, $E_4 = E_r(+) + E_r(-)$, which contains lattice and molecular terms associated with structural changes upon ionization. It is related to the outer- and inner-shell reorganization in Marcus theory.

Significant energy parameters concern (i) the exciton binding energy, E_b , representing the energy needed to dissociate the 1^1Bu exciton into a free electron hole pair and (ii) the band gap energy E_g which corresponds to the vertical excitation of the ground state to a free electron–hole pair.

Energy can be injected by optical ($h\nu_{\text{in}}$) or electric (e^- , h^+_{in}) input, and will be recovered either through light ($h\nu_{\text{out}}$) or through free charges (e^- , h^+_{out}). Nonradiative decays and charge trapping, which affect the efficiency of these internal conversions, will not be further considered.

A first issue concerns *the parity and symmetry of the lowest excited state*, either an odd parity 1^1Bu state or an even parity 2^1Ag state. The relative location of these states is essential for recovering the energy that originates from fast relaxation of upper excited states in the form of emitted light, since only the dipole-allowed 1^1Bu state shows efficient radiative decay. The relative position of these states is highly sensitive to bond length alternation and backbone topology. Pariser–Parr–Pople quantum mechanical calculations have shown that a strong alternation in electron-transfer integrals along a polymer chain leads, except when there is strong electron correlation, to the lowest lying singlet excited state having a dipole-allowed fluorescent relaxation path to the ground state.²⁰ Calculations on polyenes have concluded that for a relatively low conjugation length of about five conjugated units, the 2^1Ag level crosses and becomes lower than the 1^1Bu level, all the more as the conjugation length increases,²² as confirmed by the absence of fluorescence of polyacetylene.²³ In the case of PPV, the allowed 1^1Bu state

lies 0.5 eV lower than the 2^1Ag state,¹⁸ which agrees with its high fluorescence yield. In 6T, these two states are very close,²⁴ in agreement with the observed very low luminescence, and calculations predict that an increase of conjugation length should even move the forbidden 2^1Ag level further below the 1^1Bu level. The absence of photoluminescence of polydiacetylene²⁵ also agrees with calculations indicating the crossover of the excited-state energy levels.

A correlated issue concerns *the location of the excited (1Bu) state relative to the charged state*, which depends on the exciton binding energy E_b and its interplay with the net attraction energy E_3 , i.e., the stabilization energy of the charged states. A high yield of (electro)luminescence requires a large exciton binding energy, which significantly exceeds the net attraction E_3 for driving the equilibria irreversibly from charged states to the formation of excitons. The exciton binding energy, which is key for electrooptical processes, is linked in the first approximation to the intensity of electronic interactions (or electron correlation) developed in the excited state. However, electronic interactions also control the relative position of the excited 2^1Ag and 1^1Bu states, and a subtle balance exists for the electronic interactions, which must be large enough to ensure a high exciton binding energy, but not so large that the forbidden 2^1Ag state is driven below the allowed 1^1Bu state.

Thermodynamics as well as kinetics also govern the subtle interplay between charged states and exciton states. The dissociation of an electron–hole pair is generally an uphill process, whose probability is linked to the energy difference ΔE between the two states, $\nu_0 \exp(-\Delta E/kT)$. So the lower the exciton binding energy, the lower ΔE and the higher the probability of electron–hole pair dissociation. But a kinetic contribution to the probability of dissociation also exists, through the frequency term ν_0 , on the order of a phonon frequency, which expresses the competition between the dissociation process and the lifetime of the excitonic state. But the binding energy of excitons in organic materials, higher than 0.2 eV, and their low lifetime do not allow a large direct contribution to exciton dissociation. In conclusion, charged states are mostly created from higher energy states, through concerted relaxation–dissociation processes involving excited singlet and triplet states.

What are the features which will drive the equilibria toward the production of free charges and would favor the design of new photoconductors or photovoltaic devices? At excitation onset, e.g., 2.3 eV in the case of 6T, the kinetic energy of photogenerated charges is not sufficient to allow them to dissociate into free charges, as confirmed by the absence of significant luminescence quenching. Above a further excitation energy threshold, e.g., around 2.7 eV in the case of 6T, the observation of branching between fluorescence and singlet exciton dissociation clearly indicates that dissociated electron–hole pairs are produced, which can undergo an irreversible generation of free charges. Besides this energy threshold, an *important kinetic contribution* must also be taken into

account in the case of layered 2-dimensional semiconductors, e.g., 6T. As shown by electroabsorption, dissociation occurs preferentially by the hopping of a charge on a neighboring molecule belonging to an adjacent layer. This new situation must be associated with the existence of very high intralayer charge transport properties evidenced for these 2-D semiconductors. Interlayer ionization processes are completely different from in-plane ones, and the Onsager formalism no longer applies, since it assumes that the elemental hopping step by which the electron and hole diffuse to each other is much shorter than (i) the initial distance between the electron and hole and (ii) the capture distance. In the case of a lamellar structure, the distance of elementary hopping is on the order of that of the initial distance, and the charges will diffuse within each layer, all the faster since the intrinsic carrier mobility is high. Their recombination depends on the probability that they will find themselves again in the same initial geometry situation. This probability decreases very rapidly with time, and the recombination will be further hampered by the slowness of the last electron-hole recombination step. It can thus be concluded that dissociation of electron-hole pairs into free charges is a very efficient process in well-ordered 2-dimensional semiconductors.

Material Design

The above discussion allows some relationships to be drawn between the chemical structure and the electric and optical properties of conjugated materials.

Role of Structural Organization. Architectures of conjugated materials involve conjugated segments or units which are covalently assembled in the form of macromolecular chains in polymers, or assembled by van der Waals interactions in conjugated oligomers. Their structural organization is critical in terms of their electrooptical properties.

A first limiting case concerns one-dimensional or amorphous materials with large interchain distances, e.g., conjugated polymers, substituted oligomers, or J-type aggregates. The low intermolecular interactions allow the conjugated units to retain a high degree of freedom, and in the case of low electronic correlation, the allowedness of the lowest excited 1^1Bu state predicts a high luminescence yield. Furthermore, one-dimensionality and low intermolecular interactions also favor intrachain electron-hole recombination, which impedes dissociation processes into charges. Low intermolecular interactions are responsible for low charge transport efficiency, leading to limited electric characteristics, e.g., in thin film transistors. PPV and its related derivatives, conjugated oligomers substituted with bulky pendent groups, e.g., β -alkyloligothiophenes, are representative of this class of materials.

The other limiting case concerns highly organized 2-dimensional architectures, e.g., H-type aggregates characterized by small distances between conjugated systems, which are very common among molecular materials. The strong intermolecular interactions are responsible for the splitting of excited levels into excitonic bands, with a

forbidden, or weakly allowed, lowest excited state, which leads to the collapse of their luminescence properties. Strong intermolecular coupling also leads to the mixing of charge-transfer states with Frenkel excitons, which open new channels for the decay of upper excited states into ion pairs and further into free charges, and into triplet states. These 2-dimensional or lamellar conjugated materials also show a high anisotropy of electrooptical properties, with an interlayer dissociation of electron-hole pairs, followed by a fast intralayer diffusion of charges which dominates over radiative decays. Well-defined H-type aggregates, e.g., oligothiophenes, perylenes, polycenes, and phthalocyanines, are good examples of this class. Very attractive photoconducting and photovoltaic properties have been demonstrated for these conjugated materials, e.g., a quantum yield for conversion of almost 100% under low-power monochromatic light for polythiophene,²⁶ and also energy conversion yields of 0.006 and 0.01 in the case of photovoltaic cells based on phthalocyanines²⁷ and octithiophene,²⁸ respectively, which are the highest ever reported for organic semiconductors. Charge transport is also very efficient, the highest carrier mobilities on the order of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, being obtained with oligothiophenes and pentacene. Equilibria between excitonic states and charged states are predominantly shifted toward the generation and transport of charges, which makes molecular materials based on planar conjugated oligomers very well designed for electric devices, e.g., thin film transistors, and also for optoelectric conversion of energy.

Role of Electronic Contributions. Although one-dimensional materials appear well adapted for luminescence instead of charge generation, radiative decay of the excitonic state depends on the symmetry of the lowest excited state, either an allowed 1^1Bu state, or a forbidden or very weakly allowed 2^1Ag state. It has been shown theoretically that the relative position of these two excited states is governed by bond length alternation and electron correlations. If these interactions are too strong, the Ag level becomes located below the Bu level, leading to the extinction of luminescence. This is the worst situation, in which excitonic states are favored instead of charged states, but as luminescence is not allowed, excitation is mainly consumed in nonradiative decays, as shown by polydiacetylene, which shows neither photoluminescence nor photoconduction or a photovoltaic effect. But electronic interactions in excited states must be large enough to induce a significant exciton binding energy. The $2\text{Ag}-1\text{Bu}$ separation increases with the conjugation length of a polymer chain, as in polyenes, and alternation is higher in a copolymer such as PPV. Crossover of the $2\text{Ag}-1\text{Bu}$ levels occurs more readily for heteroaromatic rings than for aromatic ones, and for homopolymers versus copolymers, as shown by the much stronger luminescence of PPV than polyphenylene, and further than polythienylenevinylene. So strong alternation but subtle balance of electronic interactions in the excited states are required for electroluminescent materials. Finally, stabilization of

charged states and ion pairs can be achieved by the use of polar substituents on conjugated units.

Electronic factors also control the escape route of excited singlet states to the nonradiative triplet state, the efficiency of this intersystem crossing being mainly controlled by spin-orbit coupling, with a well-known contribution of heavy atoms (S, metal atoms), and also by a low-energy gap between the excited singlet and triplet states, as observed in the case of short conjugation lengths.

In conclusion, although this discussion must be considered as a first approximation sketch of the electrooptical characteristics of conjugated materials in terms of their molecular structure and properties, some guidelines have been drawn which could be useful for a better tuning of the chemical structure of these materials toward the envisioned device characteristics.

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