

Effect of fluorination on the electronic structure and optical excitations of π -conjugated molecules

Begoña Milián Medina and David Beljonne

Laboratory for Chemistry of Novel Materials, Center for Research in Molecular Electronics and Photonics, University of Mons-Hainaut, 7000 Mons, Belgium

Hans-Joachim Egelhaaf

Christian-Doppler Laboratory for Surface Optical Methods, Johannes-Kepler University, 4040 Linz, Austria and Institute for Physical and Theoretical Chemistry, University of Tübingen, 72076 Tübingen, Germany

Johannes Gierschner^{a)}

Laboratory for Chemistry of Novel Materials, Center for Research in Molecular Electronics and Photonics, University of Mons-Hainaut, 7000 Mons, Belgium and Institute for Physical and Theoretical Chemistry, University of Tübingen, 72076 Tübingen, Germany

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Fluorination of π -conjugated organic molecules is a strategy to obtain possible *n*-type conducting and air-stable materials due to the lowering of the frontier molecular orbitals (MOs) by the high electronegativity of fluorine. Nevertheless, the resulting optical gaps may be widened or narrowed, depending on the molecular backbone and/or the number and position of the fluorine atoms. The authors have performed time-dependent density functional theory calculations to address the subtle influence of fluorine substitution on the absolute MO energies and the subsequent impact on the optical transitions in homologous conjugated oligomers based on thiophene and acene units. © 2007 American Institute of Physics. [DOI: 10.1063/1.2713096]

Among the most detrimental problems associated with the wide-spread application of polyconjugated organic materials in optoelectronic devices is the unsatisfactory stability against oxygen attack.¹ In this context, (partial) fluorination of the molecular backbone is discussed as a possible solution: the high electronegativity of the fluorine atom results in a large stabilization of the highest occupied molecular orbital (HOMO) [and lowest unoccupied molecular orbital (LUMO)] levels of the materials, thus improving their stability against oxidation.^{2–5} For the same reason, perfluorination turns out to be a good strategy to produce *n*-channel organic field-effect transistors since it is an effective strategy to convert *p*-type organic semiconductors into *n*-type ones.^{6–9} Furthermore, fluorination critically influences the supramolecular organization of the molecules, which is crucial for device performances: fluorination allows to switch supramolecular organization from herringbone arrangements to π -stacks,^{2,7–15} which is favorable both for energy and electron transport.^{16,17}

The effect of fluorination on the electronic levels—and subsequently on the optical transitions—is, however, not yet fully understood. On the one hand, optical absorption and emission spectra of several fluorinated oligomers have been recently reported, where considerable bathochromic (red-) shifts against the unsubstituted species are found in alternating hydrocarbons such as perfluoro-oligoacenes (PF-*n*Ac, see Fig. 1),^{7,18} porphyrins,¹⁹ and polydifluoropyrrole.²⁰ On the

other hand, significant hypsochromic (blue-) shifts are observed in perfluorinated oligothiophenes (PF-*n*T, see Fig. 1)^{8,21} and perfluoroarene-thiophenes.¹⁶ Moreover, in multi-substituted benzenes,²² in azulene²³ and in distyrylbenzene (DSB),^{13,17,24} either blue- or redshifts are observed depending on the position of fluorine substitution. Furthermore, fluorine substitution might affect not only the energy positions but also the intensities (and/or orientations) of higher electronic (S_0 - S_n) transitions.^{7,13} Although the specific impact of fluorination on the electronic levels and transitions has often been highlighted on the basis of experimental and/or theoretical data,^{3,25} the origin of the striking differences among the various molecular backbones is still unclear. Possible explanations include intertwined effects such as geometrical deformation due to steric hindrance,^{5,8} different energetic positions of the frontier MOs of the conjugated backbone relative to the fluorine p_z orbitals,²⁶ electron correlation effects, dual electron donating/withdrawing character of the fluorine atoms,²⁶ and the relative weights of linear combination of atomic orbital (LCAO) coefficients in the given MOs.^{23,25}

We show here that none of these effects alone is able to account for all the observed trends in the electronic and photophysical properties with substitution, thus obstructing an easy-to-use intuitive analysis of the results. We demonstrate that only well-selected quantum-chemical methods, e.g., time-dependent density functional theory (TD-DFT), are capable of reproducing all the different effects of fluorination on the electronic levels and optical excitations in the different classes of molecular backbones. Thereby, we offer a re-

^{a)}Author to whom correspondence should be addressed. Electronic mail: johannes@averell.umh.ac.be

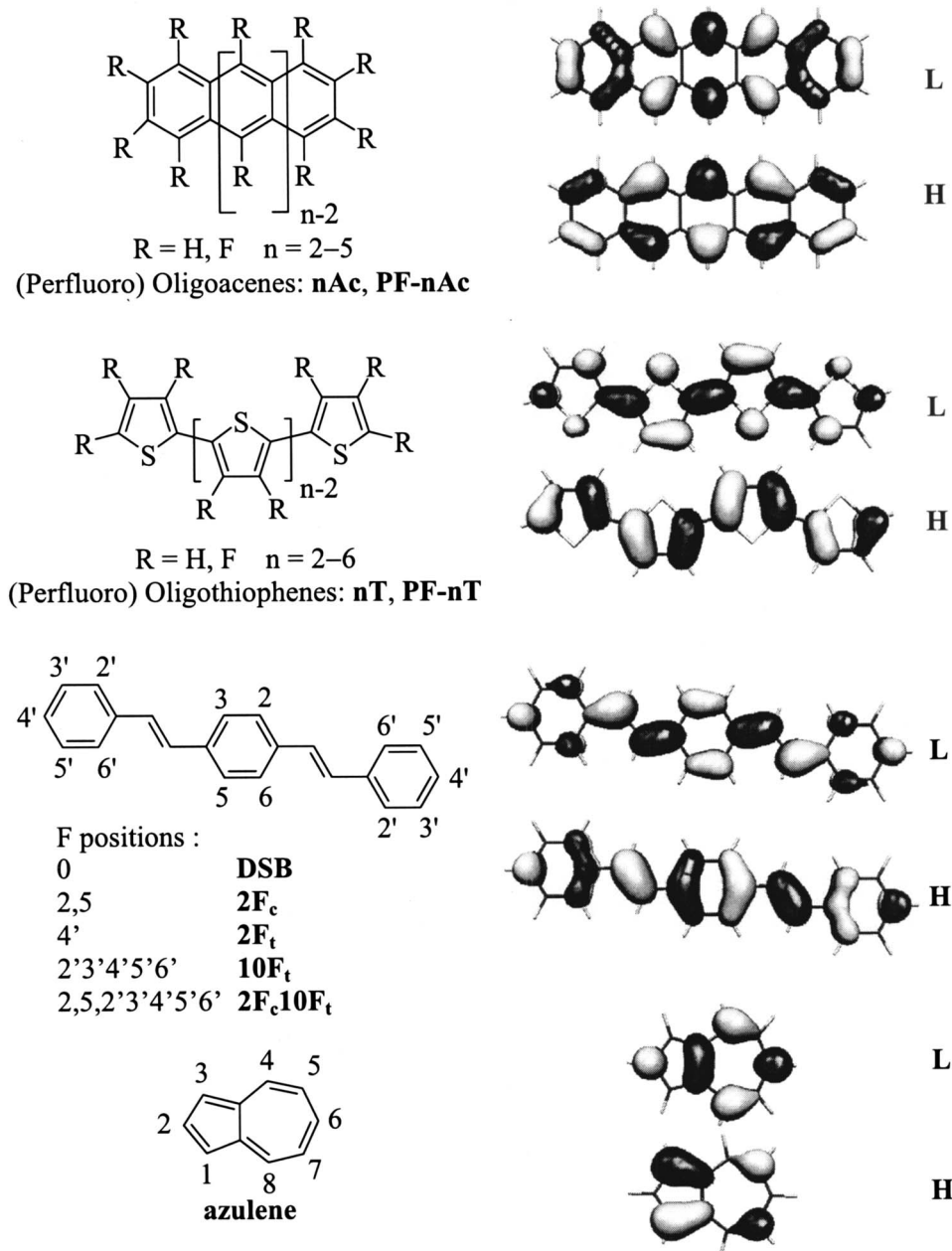


FIG. 1. Structures and electronic density contours ($0.03 e/\text{bohr}^3$) calculated for the HOMO and the LUMO of the molecules considered in this study (Ref. 34).

liable methodology to guide molecular design. Among the variety of molecules, we have chosen 6T, 5Ac, and DSB, which represent different classes of molecular backbones and opposing effects upon fluorination. The study is completed by a systematic investigation on chain-length effects. The (TD-) DFT calculations at the B3LYP/6-311G* level of theory are compared to other theoretical methods, including the semiempirical ZINDO/S method,²⁷ and *ab initio* Hartree-Fock (HF) calculations, coupled to a configuration interaction singles (CIS) scheme.²⁸ All calculations assume planar conformations of the molecules.

From experiment, a considerable blueshift of the intense low-energetic optical absorption band by $+1500 \text{ cm}^{-1}$ for PF-6T relative to 6T is found (see Table I),⁸ while a redshift of the same amount is observed for 5Ac upon fluorination.⁷ According to TD-DFT calculations, this band is assigned to the $S_0 \rightarrow S_1$ transition, which is described primarily by the

HOMO-LUMO (H-L) excitation with a contribution of more than 95%. Inspection of Table I reveals that the batho- and hypsochromic spectral shifts are largely due to the changes in the H-L energy gaps of PF-5Ac and PF-6T with respect to the unfluorinated compounds. Electron correlation also contributes to the spectral shifts but to a much lesser extent. The sign of the shift is therefore attributed solely to different stabilization energies of the H and L orbitals upon fluorination. The stabilization of the H and L levels arises from the high electronegativity and the presence of low-lying p_z orbitals of fluorine and amounts to several thousand wave numbers, see Table I. To figure out whether the absolute positions of the H and L energies against $p_z(\text{F})$ are responsible for the sign of the change of the H-L band gap, we have calculated the effect of fluorination on the series of nT and nAc oligomers. Although the frontier orbitals in both series have comparable energies (e.g., compare 5T and 4Ac in Fig. 2), the

TABLE I. Calculated (TD-DFT, ZINDO/S, and HF/CIS) and experimental values for the vertical (E_{vert}) and adiabatic (E_{adiab}) electronic transition energies and the TD-DFT frontier MOs of 6T, PF-6T, 5Ac, and PF-5Ac. Δ is the difference with respect to the reference.

10^3 cm^{-1}	6T (ref)	PF-6T	Δ	5Ac (ref)	PF-5Ac	Δ
HOMO	-39.8	-45.5	-5.7	-38.3	-45.9	-7.6
LUMO	-18.6	-23.6	-5.0	-20.6	-29.7	-9.1
GAP ^a	21.2	21.9	+0.7	17.7	16.2	-1.5
E_{vert} (TD-DFT)	19.0	20.0	+1.0	15.5	14.0	-1.5
E_{adiab} (TD-DFT)	17.7	18.7	+1.0	14.3	12.7	-1.6
E_{vert} (ZINDO/S)	19.2	18.7	-0.5	19.1	17.8	-1.3
E_{adiab} (HF/CIS)	26.3	28.4	+2.1	22.9	22.4	-0.5
E_{adiab} (Expt.)	19.7 ^b	21.2 ^b	+1.5	16.9 ^c	15.4 ^c	-1.5

^aGAP=LUMO-HOMO.

^bIn CHCl_3 , Ref. 8.

^cIn 1,2-dichlorobenzene, Ref. 7.

two types of molecules behave distinctively different upon fluorination. The PF- n Ac's exhibit bathochromic shifts whereas the PF- n T's show hypsochromic shifts at all n , see Table II. The only substantial change within the homologous series is a systematic decrease of the difference between the changes in the H-L gap and the changes in the vertical transition energies with increasing n (Table II).

The answer to the different behaviors of the PF- n Ac and PF- n T oligomer series must therefore be found elsewhere. Geometrical constraints, which lead to nonplanar structures and consequently to a spectral blueshift, can be excluded for the series of PF- n T, since the effect is already present for the calculated planar geometries. Hence, the reason must be seen in the interplay of the electron donating/withdrawing effects of fluorine with the specific molecular backbones. In the chemistry of aromatic compounds the concept of inductive ($\pm I$) and mesomeric ($\pm M$) effects is widely used in a qualitative manner to distinguish between the different contributions of the net polar effect of a given substituent.³⁰ Among all possible substituents, fluorine is the only one whose electron withdrawing inductive ($-I$) effect is strong enough to compensate the electron donating mesomeric ($+M$) effect, allowing for a subtle interplay with the parent molecular

backbone. The large $-I$ effect is related to fluorine's high electronegativity and will strongly depend on the number of fluorine atoms grafted on the conjugated backbone. The $+M$ effect shows up in the tendency for the electrons of the substituent to enter into conjugation with the π electrons of the molecular backbone and strongly depends on the position of the fluorines.^{31,32}

For alternating hydrocarbons, i.e., for molecules with a strict symmetry relation of all occupied and unoccupied MOs ($H-n$ and $L+n$, $n=0,1,\dots$), the experimental shifts can be qualitatively explained in a simple Hückel picture by describing inductive and mesomeric effects via first and second order perturbation theory.³⁰ A facile calculation³³ shows that the first order inductive effect leads to stabilization of the H and L orbitals by the same amount of energy due to the fact that the moduli of the AO coefficients in H and L are equal for a given C atom (see 5Ac in Fig. 1). However, the mesomeric effect leads to a much stronger destabilization of the H with respect to the L orbital due to the low-energetic position of the p_z orbitals of fluorine (below the H orbital of π -conjugated hydrocarbons). Thus an overall narrowing of the H-L gap is expected. For PF-5Ac,⁷ this simple picture agrees very well with the results of a TD-DFT calculation,

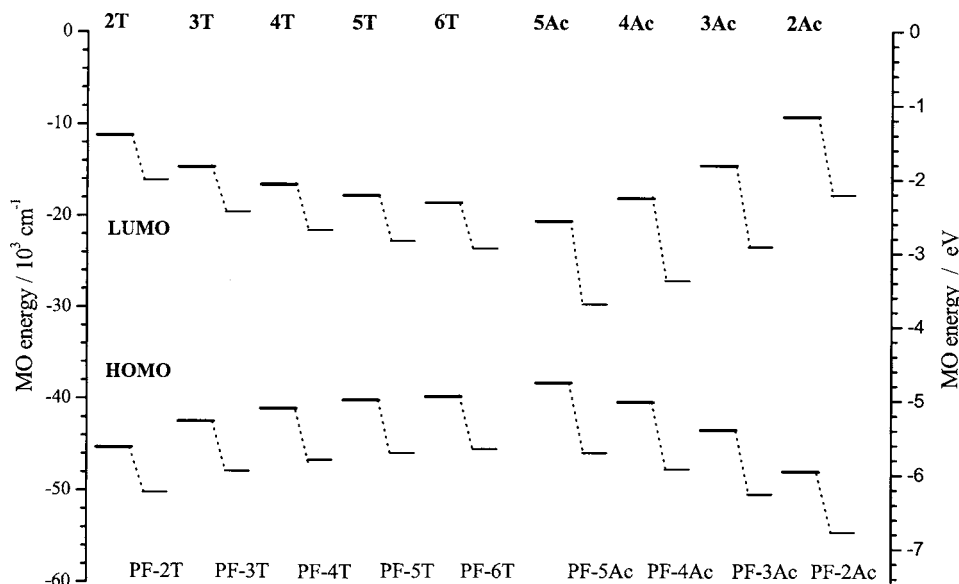


FIG. 2. Stabilization of the H, L levels upon fluorination in the homologous series n Ac and n T, as calculated at the B3LYP/6-311G* level of theory.

TABLE II. Energy shifts (in cm^{-1}) in nT and nAc upon fluorination, calculated at the TD-DFT level: change in the H-L band gap ΔE_{H-L} , change in the vertical transition energy ΔE_{vert} , and the difference $\Delta\Delta E$ between them.

	ΔE_{H-L}	ΔE_{vert}	$\Delta\Delta E$
2T	0	+700	+700
3T	+500	+1000	+500
4T	+600	+1000	+400
5T	+800	+1000	+200
6T	+700	+1000	+300
polymer ^a	+900	+1000	+100
2Ac	-1900	-1500	+400
3Ac	-1900	-1700	+200
4Ac	-1700	-1600	+100
5Ac	-1500	-1500	± 0

^aThe polymer values were obtained by Kuhn's extrapolation method, Ref. 29.

see Fig. 2. As the change in the H-L gap dominates all other effects, the H-L transition is redshifted, which is consistent with the experimental data for PF-5Ac (and many other alternating hydrocarbons).

For nonalternating π -conjugated molecules, the situation is less simple. The perfluorinated oligothiophene PF-6T is a typical representative of this group of molecules: owing to the introduction of sulfur into the molecular backbone, the electron-hole symmetry is lost. Due to the nodal planes through the sulfur atoms in H, the moduli of the LCAO coefficients on the (F-carrying) C atoms are larger in H than in L (Fig. 1). This leads to a stronger stabilization of H by the $-I$ effect than of L, different from the situation in alternating hydrocarbons. The $+M$ effect again destabilizes H more than L. The overall impact of fluorine substitution on the H-L gap thus arises from a subtle interplay between the $-I/+M$ effects, which is, however, not possible to disentangle at the simple Hückel level coupled to perturbation theory. This prevents from drawing any qualitative conclusion.

Obviously, in order to obtain better predictions, one has to turn towards more sophisticated quantum-chemical methods. Although the semiempirical ZINDO/S method reliably estimates the chain-length evolutions of optical properties (different to, e.g., TD-DFT), it faces serious problems in predicting substitution effects.²⁹ In fact, the different signs of the energetic shifts upon fluorination are not reproduced at this level of theory (Table I), independently of the applied method for geometry optimization such as AM1, HF, or DFT. *Ab initio* calculations at the HF/CIS level are able to predict the sign of the energy shifts for the perfluorinated systems.³⁵ However, the magnitude of the shift is largely underesti-

mated in the case of pentacene (Table I). Finally, time-dependent DFT is able to reproduce substituent effects in PF-5Ac and PF-6T quantitatively, see Table I. In order to test both methods for more subtle effects we have chosen multiply fluorinated DSB, as the sign and magnitude of the shift depend critically on the number and the position of the fluorine substituents: In the case where fluorine atoms are present in the central ring of DSB ($2F_c$ and $2F_c10F_t$, see Fig. 1) redshifts of -600 and -500 cm^{-1} are observed experimentally, respectively. Small blueshifts of $+100$ and $+200$ cm^{-1} are obtained for $2F_t$ and $10F_t$, respectively.^{14,17} In this case, HF/CIS fails to reproduce the sign of the shift for some substitution positions. TD-DFT turns out to be the only method, which, at a reasonable computational cost, gives the correct picture (Table III): The terminal $4'$ positions in the outer rings are rather insensitive to substitution³⁶ and the LCAO coefficients in $3'$, $5'$ positions vanish due to symmetry reasons, in both frontier orbitals (Fig. 1).¹⁷ Therefore fluorination at the outer rings cannot compete with the sensitive 2,5 positions in the central ring, which induce a bathochromic shift upon fluorination.

Another system of interest is azulene, representing a classical example of a non-alternating hydrocarbon. The TD-DFT calculation for 1,3-difluorinated azulene (Fig. 1) gives a bathochromic shift of -2900 cm^{-1} in reasonable agreement with experiment (-2320 cm^{-1}).²³ No experimental data are available for the 2,6-difluorinated species, for which a significant hypsochromic shift of $+2700$ cm^{-1} is predicted by the TD-DFT calculations. In this case, the LCAO coefficients at the positions of interest are substantially different in H and L: while in the HOMO the 2 and 6 positions correspond to nodes in the wave function and the 1 and 3 positions bear large LCAO coefficients, the situation is exactly the opposite in the LUMO (Fig. 1). Thus, from the fact that fluorination at positions 1, 3 has a bathochromic effect whereas it has the opposite effect at positions 2, 6,²³ it follows that in azulene (at least for the two substitution patterns under investigation) the mesomeric effect clearly dominates the inductive one.

Fluorination also affects the polarization¹⁴ and the intensity of electronic transitions.³¹ According to the absorption spectra of 5Ac and PF-5Ac, recorded by Sakamoto *et al.*,⁷ the fluorinated compound shows an intense band located at 5700 cm^{-1} above the $S_0 \rightarrow S_1$ band, with an oscillator strength five times larger than the latter. In contrast, in the unsubstituted species 5Ac, this band is seen only as a weak shoulder 6100 cm^{-1} above $S_0 \rightarrow S_1$, almost hidden under the vibronic replica of the $S_0 \rightarrow S_1$ transition. This remarkable difference between PF-5Ac and 5Ac is again well reproduced by the TD-DFT calculations.³⁷ In both molecules, the

TABLE III. Calculated (TD-DFT, HF/CIS) and experimental values for the electronic transition energies of DSB, $2F_c$, $2F_t$, $10F_t$, and $2F_c10F_t$. Δ is the energy difference with respect to DSB.

10^3 cm^{-1}	DSB	$2F_c$	Δ	$2F_t$	Δ	$10F_t$	Δ	$2F_c10F_t$	Δ
E_{vert} (Calc.)	25.6	25.0	-0.6	25.6	0.0	25.5	-0.1	25.1	-0.5
E_{adiab} (Calc.)	23.9	23.5	-0.4	23.9	0.0	23.9	0.0	23.6	-0.3
E_{adiab} (Expt.) ^a	26.1	25.5	-0.6	26.2	+0.1	26.3	+0.2	25.6	-0.5
E_{adiab} (HF/CIS)	31.3	31.0	-0.3	31.5	+0.2	31.8	+0.4	31.6	+0.3

^aFirst fluorescence peak in cyclohexane, see Ref. 17.

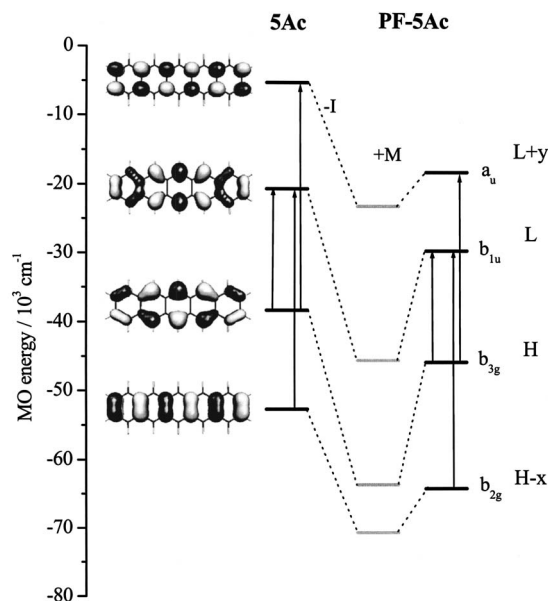


FIG. 3. Frontier MOs and electronic transitions of 5Ac and PF-5Ac, as calculated at the B3LYP/6-311G^{*} level of theory. The different contributions of the inductive ($-I$) and mesomeric ($+M$) effects are depicted schematically.

band is assigned to the $S_0 \rightarrow S_3$ transition, which is described by an out-of-phase linear combination of $H-x \rightarrow L$ and $H \rightarrow L+y$ excitations.³⁸ The resulting transition dipole moment μ is determined by the relative weights of these electronic configurations ($c_{H-x \rightarrow L}, c_{H \rightarrow L+y}$), which themselves depend on the energy difference ΔE between the involved MOs ($c_i \sim \Delta E^{-1}$). The dramatic difference in the intensities of the $S_0 \rightarrow S_3$ transitions in 5Ac and PF-5Ac arises from the very different CI contributions in these two molecules. In 5Ac, both excitations ($H-x \rightarrow L$ and $H \rightarrow L+y$) contribute similarly to the S_3 excited state ($c_{H-x \rightarrow L} = +0.52$, $c_{H \rightarrow L+y} = -0.47$), since the energetic differences $\Delta E(H-x, L)$ and $\Delta E(H, L+y)$ are almost identical (Fig. 3). Consequently, the antisymmetrical linear combination of both contributions leads to a vanishing small oscillator strength. Fluorination in PF-5Ac has a very different impact on the H, L orbitals on one side and on the $H-x$, $L+y$ orbitals on the other side. The differences result from the different topologies of these MOs. Whereas in H, L the 14 C atoms carrying fluorine show large LCAO coefficients, in $H-x$, $L+y$ only the four outer C atoms show significant contributions, see Fig. 3. This leads to a weaker stabilization due to inductive effects and a weaker destabilization due to mesomeric effects of $H-x$, $L+y$ against H, L. The overall effect is a stronger stabilization of $H-x$, $L+y$, revoking the degeneracy of the $H-x \rightarrow L$ and $H \rightarrow L+y$ electronic configurations, i.e., $c_{H \rightarrow L+y} = +0.62$ and $c_{H-x \rightarrow L} = -0.31$, respectively, and thus leading to considerable oscillator strength of the $S_0 \rightarrow S_3$ transition.

In conclusion, we have elucidated the impact of fluorination on the electronic levels and optical excitations in different classes of π -conjugated organic molecules, in homologous oligomeric series, and for multiple substitutions and positional patterns. The consequences of fluorination, leading to narrower or wider band gaps for different classes of materials and different positions of fluorine, were discussed.

The subtle interplay of the electron donating and withdrawing properties of fluorine with a given molecular backbone does not allow for an easy “intuitive” insight into the overall effect. At a quantum-chemical level, the sign and magnitude of the energy shifts in all compounds under study are only well reproduced by time-dependent DFT calculations, thus offering a useful recipe to guide future molecular design of materials with tunable LUMO levels appropriate for n -type conducting optoelectronic devices.

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- ³³For a given molecule, substitution of the H atom at the C atom ρ with a fluorine atom modifies the energy of the orbitals due to the inductive and mesomeric effects. These can be cast for a given orbital i according to perturbation theory following Eqs. (1) and (2), where $\Delta\varepsilon_{\text{ind}}^{(1)}$ ($\Delta\varepsilon_{\text{ind}}^{(2)}$) and $\Delta\varepsilon_{\text{mes}}$ refer to first (second) order inductive and mesomeric effects, respectively, and the symbol C-F means that the sum is extended over all carbon atoms carrying a F atom.

$$\Delta\varepsilon_{\text{ind},i} = \Delta\varepsilon_{\text{ind},i}^{(1)} + \Delta\varepsilon_{\text{ind},i}^{(2)} = \sum_{\text{C-F}} \left[c_{i\rho}^2 \Delta\alpha_\rho + \sum_{j \neq i} \frac{c_{i\rho}^2 c_{j\rho}^2 \Delta^2 \alpha_\rho}{\varepsilon_i - \varepsilon_j} \right], \quad (1)$$

$$\Delta\varepsilon_{\text{mes},i} = \sum_{\text{C-F}} \frac{c_{i\rho}^2 c_{k\sigma}^2 \Delta^2 \beta_{\rho\sigma}}{\varepsilon_i - \varepsilon_k}. \quad (2)$$

- Here $c_{i\rho}$ is the LCAO coefficient at the C atom ρ in the MO i in the unsubstituted molecule, $\Delta\alpha_\rho$ is the change in the Coulomb integral of C atom ρ due to the inductive effect of the F, ε_i and ε_j are the energies of the MOs i and j in the unsubstituted molecule, $c_{k\sigma}$ is the LCAO coefficient of F atom σ in its $2p_z$ AO k , and $\Delta\beta_{\rho\sigma}$ is the resonance integral between the F atom σ and the C atom ρ . [It should be noted that Eqs. (1) and (2) are strictly correct within the zero differential overlap level of theory only for monosubstitution. For multisubstituted molecules the expressions are approximations, due to the non-additivity of second order perturbation effects.] The balance between these effects will determine the sign of the shift. Due to the electron withdrawing character of the fluorine atom, the inductive effect will always lead to a stabilization of both H and L, whereas the mesomeric effect will always destabilize the frontier MOs due to the low-lying $2p_z$ AO of fluorine.
- ³⁴The MOs have been depicted using the MOLEKEL 4.3 program by P. Flükiger, H. P. Lüthi, S. Portmann, and J. Weber, Swiss Center for Scientific Computing, Manno, Switzerland, 2002; S. Portmann and H. P. Lüthi, *Chimia* **54**, 766 (2000).
- ³⁵The comparison between HF/CIS and experimental energies was done in terms of adiabatic transition energies since vertical transition energies are largely affected by a bad description of the potential energy hypersurface of the excited state at the CIS level.
- ³⁶J. C. Sancho-García, L. Poulsen, J. Gierschner *et al.*, *Adv. Mater. (Weinheim, Ger.)* **16**, 1193 (2004).
- ³⁷The relations between the oscillator strengths (f) $f(S_0 \rightarrow S_3)/f(S_0 \rightarrow S_1)$ are 0.2 in 5Ac and 8 in PF-5Ac at the B3LYP level.
- ³⁸In the case of 5Ac the orbitals involved are H-2 and L+2, whereas in PF-5Ac they are H-3 and L+1. Since in both molecules H-2 and H-3, on the one hand, and L+2 and L+1, on the other hand, correspond to the same type of MOs (b_{2g} and a_u , respectively), we have adopted the notation H- x and L- y for simplicity.