

Evaluation of the electronic properties of hybrid semiconducting organic-fullerene materials

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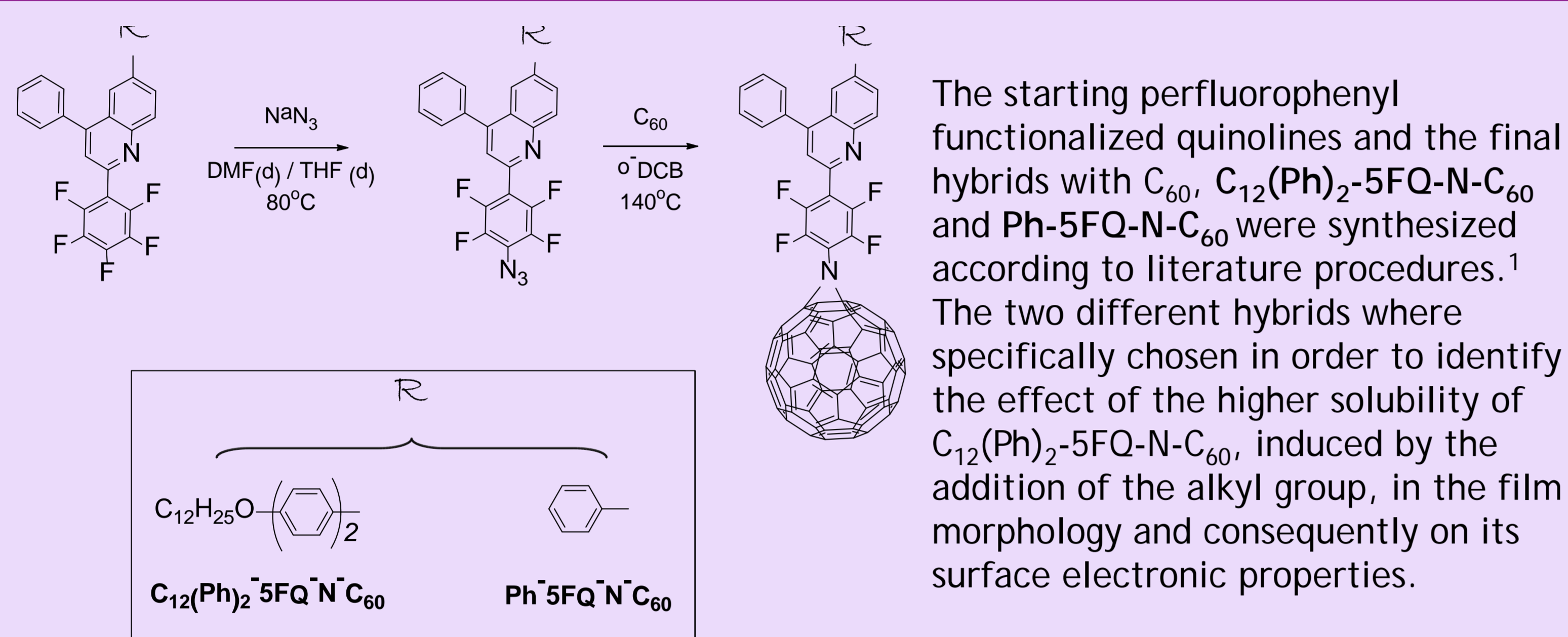
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Introduction

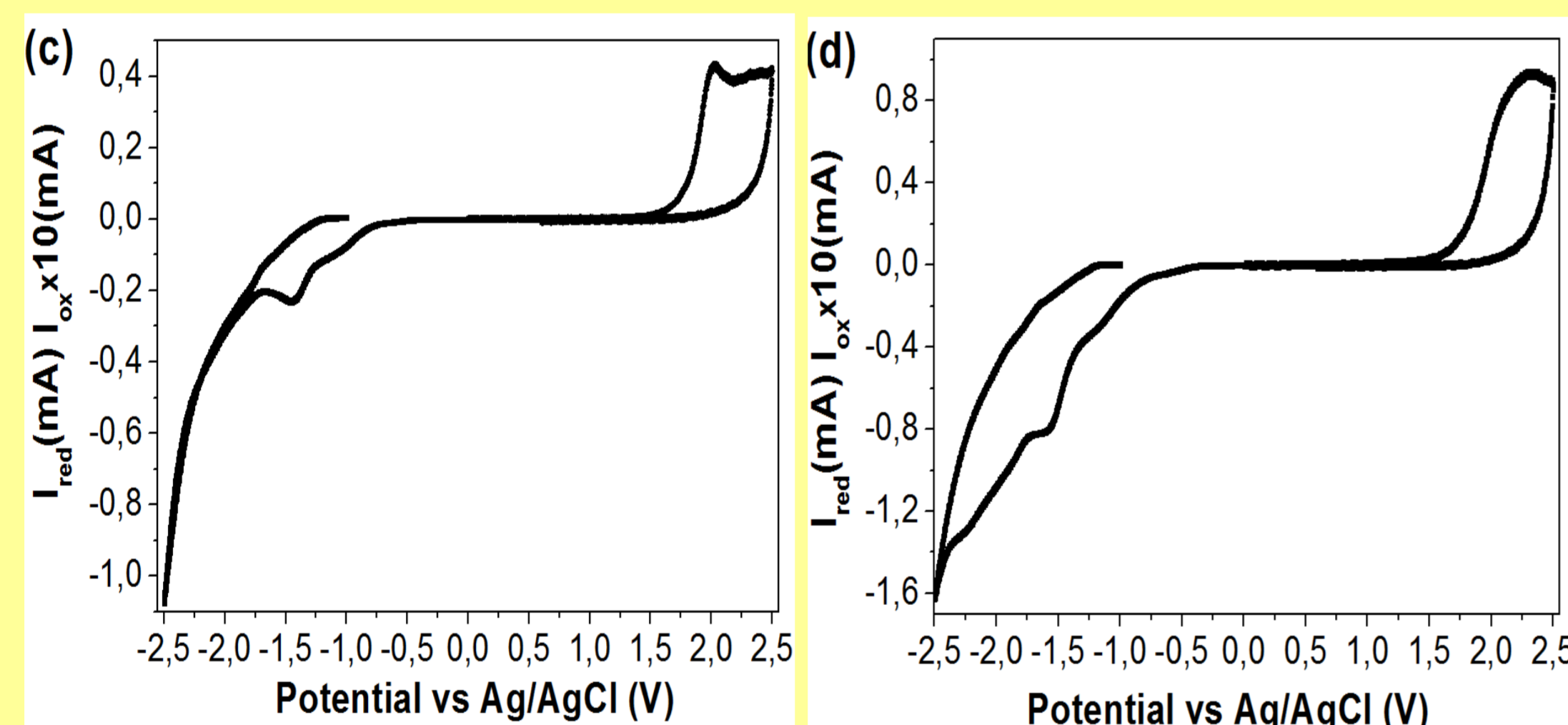
An efficient methodology has been recently reported by our group for the direct attachment of perfluorophenyl functionalized organic moieties, small molecules, polymer or copolymers, onto the sp² hybridized surface of fullerene species. The novelty of this route lies in the conjugated interconnecting part placed in-between the semiconducting moiety, here electron accepting quinolines, and the carbon nanostructure. This method could enhance electronic interactions between the two counterparts possibly creating novel hybrid systems with unique integrated properties. The hybrid molecules were prepared via a two-step reaction sequence (**Scheme 1**). The electronic structure of the valence band and the surface electronic properties of the materials in the form of thin films developed on Si and ITO coated glass substrates were studied by X-Ray and Ultraviolet Photoelectron Spectroscopies (XPS/UPS) whereas the band gap was determined by Cyclic Voltammetry (CV). The ultimate scope of this work is the elucidation of the molecules' potential application as electron acceptors in organic photovoltaic solar cells (OPVs).

Synthetic procedure of perfluorophenyl phenylquinoline hybrid molecules with C₆₀.



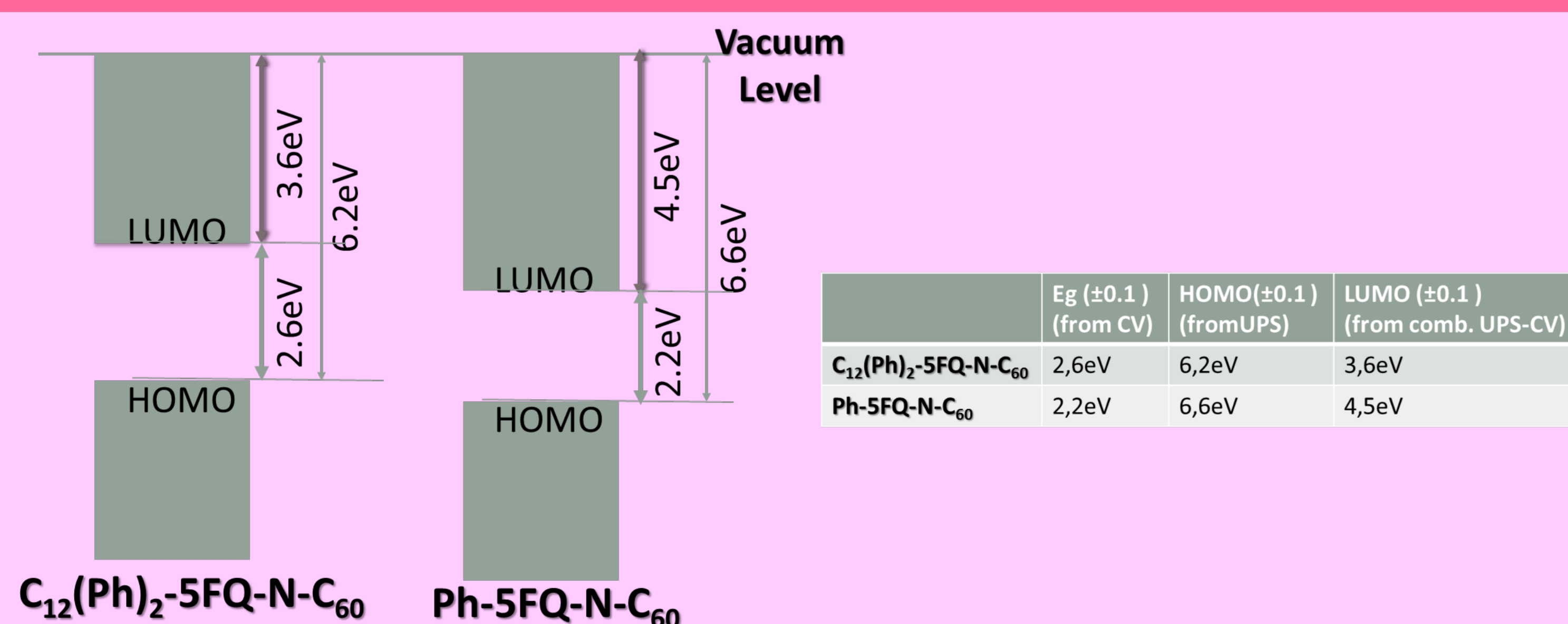
Cyclic-Voltammetry Graphs

The cyclic voltammetry curves of C₁₂(Ph)₂-5FQ-N-C₆₀ and Ph-5FQ-N-C₆₀, are presented in Fig. 1c and 1d, respectively. One irreversible oxidation and two irreversible reduction peaks were observed. For C₁₂(Ph)₂-5FQ-N-C₆₀ the onset potentials for oxidation and reduction are +1.8V and -0.8V respectively, vs Ag/AgCl. For Ph-5FQ-N-C₆₀ the onset oxidation and reduction potentials are +1.8V and -0.4V, respectively. The electrochemical band gap was evaluated according to the following equation: $E_g = e(E_{ons}^{ox} - E_{ons}^{red})$



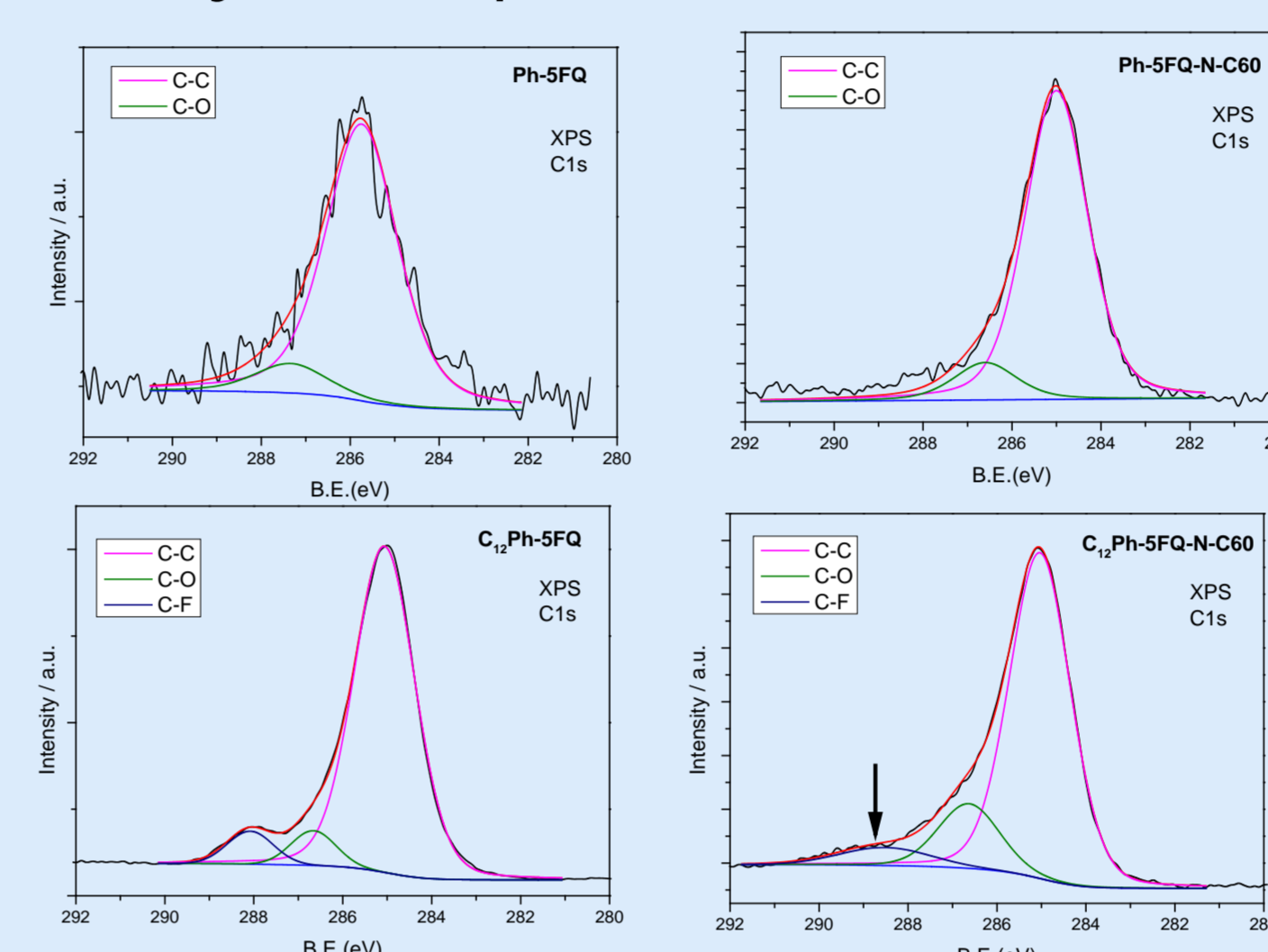
Cyclic voltammograms of (c) C₁₂(Ph)₂-5FQ-N-C₆₀, (d) Ph-5FQ-N-C₆₀ on ITO. Scan rate 01V/s.

UPS - CV results were combined to determine the electronic band structure of the materials



X-Ray and Ultraviolet photoelectron Spectroscopies

XPS of C1s peaks of monomer and monomer-C₆₀ (hybrid) samples on Si substrate.

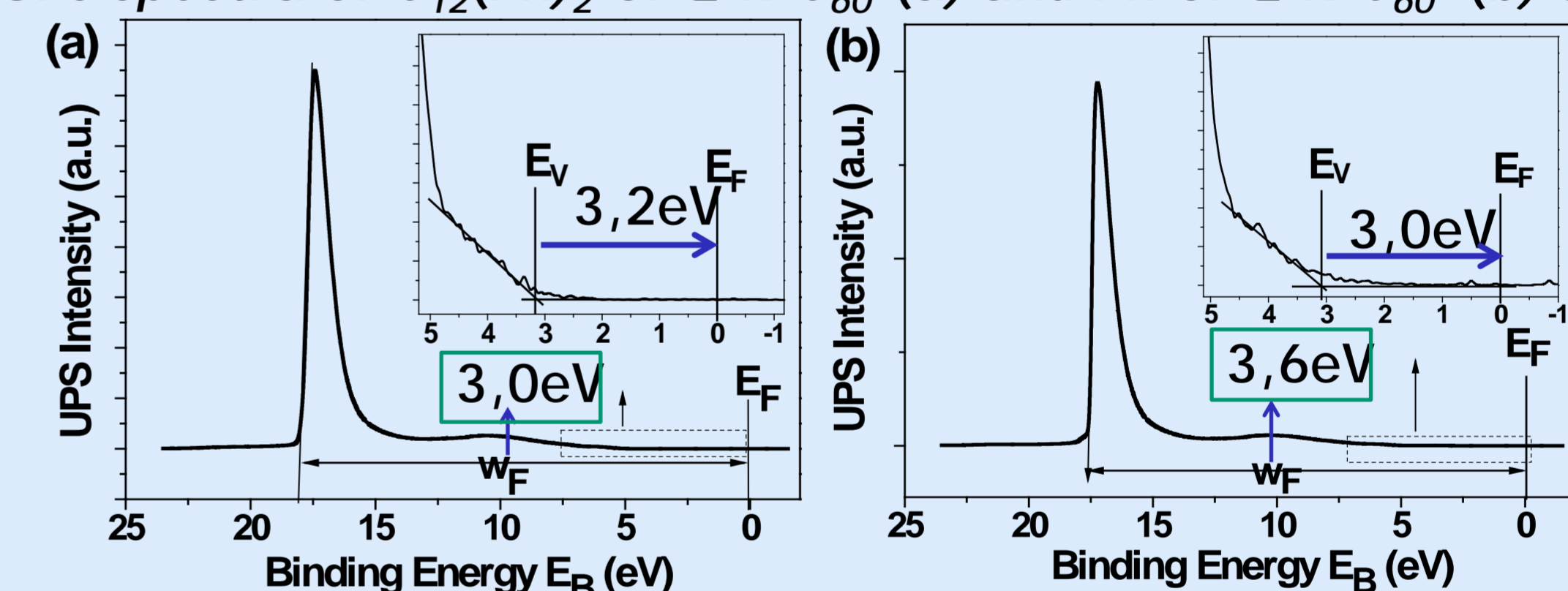


The surface F/C atomic ratios of both samples C₁₂(Ph)₂-5FQ-N-C₆₀ and Ph-5FQ-N-C₆₀ were calculated from the F1s and C1s core level peaks and was found to be 0.0092 and 0.037(± 10%), respectively. The latter value is close to the nominal one for Ph-5FQ-N-C₆₀ but the former is much lower than the nominal for C₁₂(Ph)₂-5FQ-N-C₆₀. Bearing in mind the surface sensitivity of XPS, this discrepancy clearly indicates that the surface ends in a layer of carbon atoms most probably a layer of fullerene units.

Table: Atomic ratio F/C for the monomer and monomer-C₆₀ (hybrid) samples as derived from the XPS intensity of the F1s and C1s. The nominal ratio is in brackets

	Ph-5FQ	Ph-5FQ-N-C ₆₀	C ₁₂ (Ph) ₂ -5FQ	C ₁₂ (Ph) ₂ -5FQ-N-C ₆₀
F/C atomic ratio	0.13 (0.15)	0.037 (0.043)	0.13 (0.11)	0.0092(0.038)

He I UPS spectra of C₁₂(Ph)₂-5FQ-N-C₆₀ (a) and Ph-5FQ-N-C₆₀ (b) on Si.



The HOMO level of C₁₂(Ph)₂-5FQ-N-C₆₀ and of Ph-5FQ-N-C₆₀ can be determined from the analysis of the UPS spectra where two regions are significant:

❖ The region near the Fermi level (near 0eV) where the valence band maximum relative to the Fermi level can be determined (E_v).

❖ The high binding energy cutoff, (right side in the figures) where the W_F value can be derived. The HOMO level is calculated by adding the absolute values of the measured work function and the E_v and the results are:

✓ the HOMO level for C₁₂(Ph)₂-5FQ-N-C₆₀ is 6.2 eV, very close to that of C₆₀ (6.1 eV) in agreement with the XPS findings that show a fullerene terminated surface.

✓ the HOMO level for Ph-5FQ-N-C₆₀ is 6.6eV, higher than C₁₂(Ph)₂-5FQ-N-C₆₀ originating, as the XPS results indicate, from a more mixed surface composition as opposed to the layered structure of C₁₂(Ph)₂-5FQ-N-C₆₀.

Conclusions

- The combination of photoelectron spectroscopies and cyclic voltammetry provided significant insight in the investigation of the band structure and electronic properties of thin hybrid layers
- The higher solubility of C₁₂(Ph)₂-5FQ-N-C₆₀ due to the addition of the alkyl chain appeared to lead to more homogenous distribution of the film on the substrate's surface. The C₆₀-terminated surface resulted in HOMO values very close to that of the fullerene species while the Ph-5FQ-N-C₆₀ surface appeared to have a higher HOMO value originating, from a more evenly mixed surface composition.
- These observations should be taken into account when considering the potential of these materials for use as electron acceptors in OPVs.

Relative literature

- [1] S. Kakogianni, et. al. J. Mater. Chem A, 2; 8110, (2014).
- [2] M. Yan, et. al. J. Org. Chem. 59; 5951 (1994).
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Acknowledgements

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