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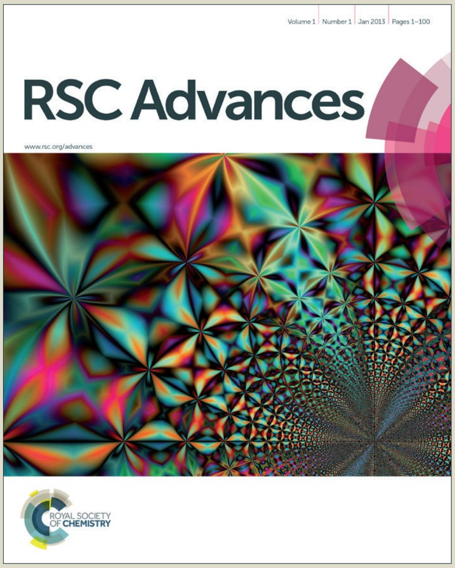

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Graphene-based acceptor molecules for organic photovoltaic cells: a predictive study identifying high modularity and morphological stability

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Ideal donor:acceptor pairs are required to improve organic photovoltaic lifetimes and efficiencies. Here an idealized donor:acceptor for organic solar cells is predicted. Circular and triangular graphene-based hexabenzocoronenes are shown, in conjunction with the energetically well-placed poly(3-oxypentylthiophene), to provide requisite HOMO/LUMO levels for efficient charge transfer through columnar structures and hole/electron extraction. Circular hexabenzocoronenes are furthermore adaptable to energy-level modulation by targeted substitutions.

The search for new donor:acceptor pairs for organic photovoltaic (OPV) applications is highly important for socio-economic and environmental reasons. From the point of view of performance and stability, the composite of poly(3-hexylthiophene):[6,6]-phenyl-C_{61}-methylbutyrate (P3HT:PCBM), Figure 1a, has long been the standard bearer.[1-4] However, the poor electronic correlation between the donor (P3HT) and the acceptor (PCBM), combined with numerous morphological instabilities are two of the major problems that are tackled through diverse solutions proposed in the literature.[5-7] The search for a better correlation in the electronic properties ranges from minor modifications in the chemical structures of one of the components to a complete replacement of the donor or acceptor molecule.[8-19] Due to the inherent difficulties of synthesizing or grafting groups onto fullerene, the precursor of PCBM, numerous authors have sought to replace it.[19] Graphene-based materials[8,19,21-23] have rapidly appeared as good acceptor candidates, primarily because of their remarkable semiconducting properties.[23]

Materials in organic photovoltaic (OPV) cells should ideally be adapted and optimized for maximum efficiency at each stage of the process of converting solar energy into electricity. The key parameters to be optimized are briefly summarized in Figure 1a, based on a comparison between the band-structure of P3HT:PCBM and that of an ideal donor:acceptor pair.[24] They are: i) The energy difference between the LUMO of the donor and the LUMO of the acceptor (DE^{LUMO}), which should be of the order of 0.3 eV to ensure ideal efficiencies during electron transfer.[25] This value is sufficient to provoke ultra-fast electron transfer from the donor to the acceptor and cannot be reduced due to the possibility of charge transfer reversal. ii) The bandgap (E_g) of the donor molecule should be close[3] to 1.5 eV. For P3HT this value is about 1.9 eV and thus too high, limiting light absorption.[26] iii) The open circuit voltage (V_{oc}) must be adjusted: if too high, considerable energy is lost; if too low, the OPV would work at an unnecessary low voltage, making potential energy conversion inefficient.

This work quantifies the results of an exploratory theoretical study on functionalized, exemplar graphene-based materials, namely hexabenzocoronenes (HBCs), checking the suitability of the whole set of parameters that govern the efficiency of the OPV device from both electronic and oxidative stability points of view. If one of these self-assembled HBCs was proven to have the expected electronic properties for OPV,[27] it would be superior to PCBM by way of its two-dimensionality, its avoidance of micro-aggregations disrupting the morphology and rupturing the active layer and the device,[28] and its ability to increase exciton pathway lengths and facilitate charge transport. By its columnar structure it should channel charges and thus enable diffusion to the electrode through a favorable graphene/electrode interaction.[29-31] This work continues that with the donor P3HT as a theoretical study to guide syntheses towards donor:acceptor pair(s) with properties optimized for use in OPVs. The results presented in this work point in the same direction as experimental work described by Yan *et al.*,[23] and reinforce the notion that theoretical modeling is an indispensable tool when searching for optimized materials.

The synthetic procedure to obtain HBCs can lead to either circular (*circ*-HBC) or triangular (*tria*-HBC) forms, the latter having already been used in the active layer of a bulk heterojunction device.[32,33]

Both *circ*-HBC and *tria*-HBC are examined in this theoretical study. Our objective is to find an acceptor with electronic properties that match the donor by appropriate chemical functionalization of these structures. We have therefore studied four substituents (see Table 1), of different size and nature. The first three were chosen for their electron-withdrawing character i.e., $-CO_2H$, $-CO_2C_4H_9$ and $-CO_2C_6H_{13}$. These substituents modulate the electronic position of the LUMO's acceptor according to the electronic HOMO-LUMO electronic position of the selected donor. Moreover, their increasing size permits an understanding of steric effects. The fourth, $-C_6H_{13}$ acts as an electron donor and was studied because of its wide use as an moiety increasing the solubility of the graphene-based molecules. Moreover, owing to both the two-dimensional structure of these systems and possible hydrogen-bond formation between substituents of two consecutive planes, a specific conformational study has been conducted to evaluate the rotation angle α adopted by the substituents with respect to the hexabenzocoronene (HBC). These results (see SI) will be used as a basis for the molecular dynamics hereafter described.

The calculated HOMO and LUMO energies of two donor systems (P3HT and P3OPT) with the various acceptors (two-dimensional HBC) are given in Table 1 and Figure 1b. P3OPT is used as it has a reduced intrinsic bandgap of 1.4 eV,[23] making it possible to attain the theoretically optimized value of 1.5 eV, and is expected to demonstrate high photo-[25] and photo-oxidative[34] stability. In addition, P3OPT should give rise to a greater electronic delocalization which can favor the transfer of charges between the donor and the acceptor. The chosen acceptor, two-dimensional HBC also shows a greater electronic delocalization than that of PCBM due to the accessibility of the π-orbitals. As a consequence, the global delocalization of electrons over the whole donor:acceptor system favor charge transfers.[30]

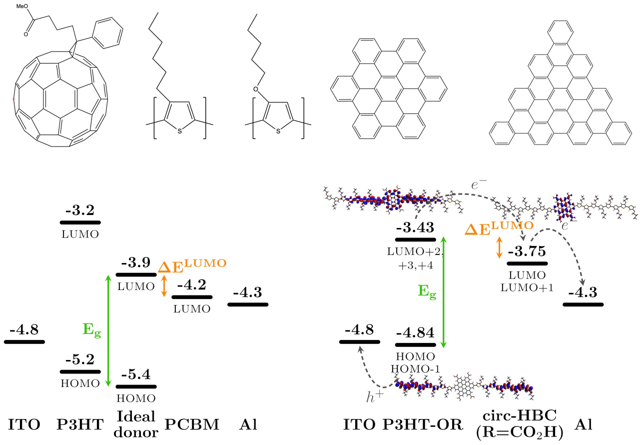


Fig. 1. Top (1a), structures discussed, from left to right: PCBM, P3HT, P3OPT, *circ*-HBC and *tria*-HBC, and below (1b), E_g, $\Delta E^{\mathrm{LUMO}}=E^{\mathrm{LUMO}}(\mathrm{donor})-E^{\mathrm{LUMO}}(\mathrm{acceptor})$. Note: given that for an ideal system, $V_{\mathrm{oc}} = 1/e\ (|E^{\mathrm{HOMO}}(\mathrm{donor})| - |E^{\mathrm{LUMO}}(\mathrm{acceptor})|) - 0.3$ V, where 0.3 V is an empirical value,[3] the parameters for E^{LUMO}(acceptor) and E^{HOMO}(donor) are shown for (left) an ideal donor:PCBM system, against (right) ideal P3OPT—*circ*-HBC(R=CO_2H)—P3OPT.

The electronic levels of grafted *circ*-HBC molecules are in good agreement with both an 'ideal electronic situation' (Figure 1b), the experimental attempt[23] and the data reported by Gupta *et al.*[22] into graphene quantum dots. Interestingly, the theoretical data gathered on HBC systems demonstrate that the shape and functionalization of these molecules lead to a wealth of possibilities to modulate the electronic properties on a wide energy range. Both triangular and circular functionalized HBCs could get close to the ideal configuration (regarding V_{oc} and ΔE^{LUMO}) to match our target donor material P3OPT, however, it is clear that *circ*-HBC, *a priori*, allows much greater modularity when grafted by electron-withdrawing substituents. The system constituted of a *circ*-HBC grafted with a CO_2H substituent combined with P3OPT as donor material were calculated to possess a ΔE^{LUMO} of 0.32 eV and an open-circuit voltage of 0.79 V. These two values, jointly to the DFT calculated HOMO/LUMO orbitals of the single P3OPT—*circ*-HBC(R=CO_2H)— P3OPT depicted in Figure 1 get very close to an ideal OPV system and provide an extremely good test candidate for future studies.

The intrinsic ability of HBC to form ordered stacks – the structure of which depends on the type of HBC substituents – is a useful property in that charge may be more easily transported to the electrodes.[29,35] We therefore carried out additional investigations on the π-stacking properties using *ab initio*, DFT and molecular dynamics (MD) simulations. While we used graphene-based acceptor molecules for the *ab initio* and DFT simulations, molecular dynamic simulations were applied to the combined donor:acceptor molecule (P3OPT—*circ*-HBC(R=CO_2H)—P3OPT, see **Figure 2**) to investigate the stability of these π-stacked arrangements of HBC molecules in solution with an organic solvent.

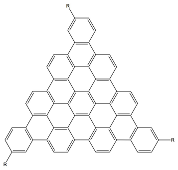
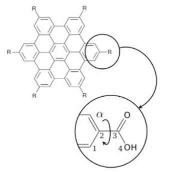
acceptor R		ΔE^{LUMO} (eV) vs. donor		V_{oc} (V) vs. donor*	
		P3HT	P3OPT	P3HT	P3OPT
	H	-0.15	-0.38	1.85	1.49
	hexyl	-0.26	-0.49	1.96	1.60
	CO_2H	0.18	-0.05	1.52	1.16
	$CO_2C_4H_9$	-0.03	-0.26	1.73	1.37
	$CO_2C_6H_{13}$	-0.03	-0.26	1.73	1.37
	H	-0.35	-0.58	2.05	1.69
	hexyl	-0.45	-0.68	2.15	1.89
	CO_2H	0.55	0.32	1.15	0.79
	$CO_2C_4H_9$	0.24	0.01	1.46	1.10
	$CO_2C_6H_{13}$	0.23	0.00	1.45	1.10
PCBM		1.00	0.77	1.00	0.64
ideal P3HT:PCBM		0.3		1.3	

Table 1. Calculated ΔE^{LUMO} and V_{oc} (V) values of the graphene-based molecules relative to those of P3HT and P3OPT donors. *Note: V_{oc} values are calculated for an ideal case and in agreement with $V_{\mathrm{oc}} = 1/e\ (|E^{\mathrm{HOMO}}(\mathrm{donor})| - |E^{\mathrm{LUMO}}(\mathrm{acceptor})|) - 0.3$ V. In general terms, one can simultaneously consider both the Coulombic energy between an ion-pair resulting from a charge transfer (estimated to be *ca*. -0.3 V by Scharber *et al.*[3]) and the counter-effect of the raise in the LUMO due to π-stacking of HBC layers. For the LUMO shift due to stacking, we have estimated it to be equal to +0.15 eV downwards when the stacking has a rotation angle of 0 °, and +0.01 eV when this angle is 17.28 ° (which correspond to the average angle extracted from our MD calculations). Its term is not reported in Table 1 but must be taken into account as a probable non negligible counter-effect in real π-stacked systems.

An evaluation and calculation of the geometrical and electronic properties was performed and compared with graphite itself.[36] The inter-HBC equilibrium distances was calculated to be 3.43 and 3.47 Å at ωB97XD/6-31G* and SAPT-DFT [PBE0/cc-πVDZ])[37] levels of calculation respectively. These results compare favorably to the inter-sheet distance of graphite (3.35 Å)[38] and also to the results reported by Mackie *et al.* using various levels of theory.[39] Further performance enhancements for OPVs are expected to be possible from directly linking donor and acceptor in a single molecule due to improved electron transfer rates. To ensure at an early stage that the changes to the HBC core do not, in principle, hinder the π-stacking, we dynamically simulate the behavior of functionalized *circ*-HBC in solution. After equilibrating the system for 1 ns (releasing more and more parts of the system), we find a π-stacked system, signaling convergence *via* energetic and structural features (see the SI). For a production run of 2.5 ns, an average distance of 3.45 Å between two *circ*-HBC molecules is obtained, which is in very good agreement with experimental[36] and theoretical results[37,40] for similar systems. The π-stacked structure remains stable throughout the whole simulation time and the stacking of the molecules is illustrated in Figure 2, providing the distribution function g_z in dependency of the z-coordinate. Further analyses on structural features are provided in the SI.

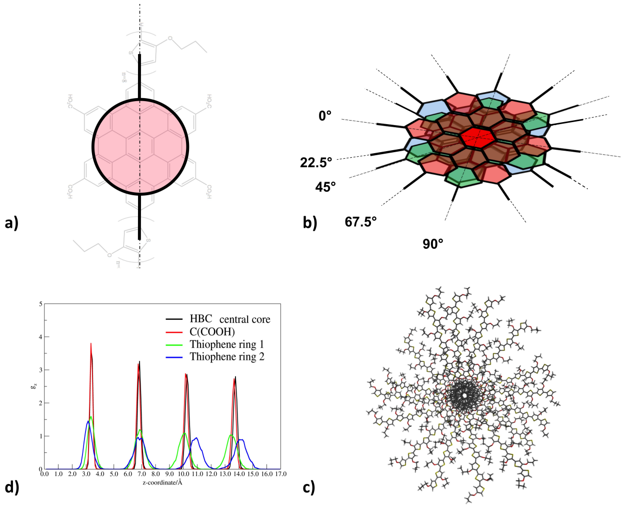


Fig. 2. a) Molecular structure of P3OPT-*circ*HBC(R=CO_2H)-P3OPT. b) Stacking pattern at the start and c) top view of the stacked molecules at the end of the MD simulation. d) Analysis of the stacking pattern. The averaged z coordinates of the central core of one HBC have been set to zero and the distribution function in z direction (g_z) of the different groups were calculated. For the core of HBC (6 atoms) and both thiophenes directly attached to the HBC (5 atoms) we averaged over the z coordinate.

A full analysis of the HBC molecules in the condensed phase as well as the electronic properties relevant for the OPV performance (including excitation, and charge transport) are beyond the scope of this study and will be addressed in future work through a systematic theoretical investigation.

To conclude, the present study aimed to optimize the electronic levels of the acceptor material with respect to the properties of the promisingly photostable P3OPT electron donor. HBC was demonstrated to be a suitable model of graphene, its size and structure being well adapted to replace PCBM because of its two-dimensionality. In addition to its electronic properties, its columnar structure (which should resolve the low efficiency observed by Gupta *et al.*[22] with graphene quantum dots) should channel the electron flux and thus enable charges to diffuse to the electrode through a favorable graphene/electrode interaction, and by way of its planarity, be resistant against oxidative processes.[41] The influence of the substitution by side chains on the energy of the LUMO level of HBC provided exactly what we were hoping to achieve: for a two component system consisting of a *circ*-HBC grafted with a $-CO_2H$ substituent as acceptor and P3OPT as donor, we obtain $\Delta E^{LUMO} = 0.32$ eV and $V_{oc} =$ around 0.8 V, both excellent values to form a an efficient solar cell. While theoretical work needs to be carried out with a wider set of substituents, this study opens the way to the optimization of new donor:acceptor pairs, individually and in combined molecules, with a high modularity to be tested in experimental OPV devices.

Notes and references

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Electronic Supplementary Information (ESI) available: *Ab-initio* and dynamic mechanical computational methodologies. This material is available free of charge via the Internet
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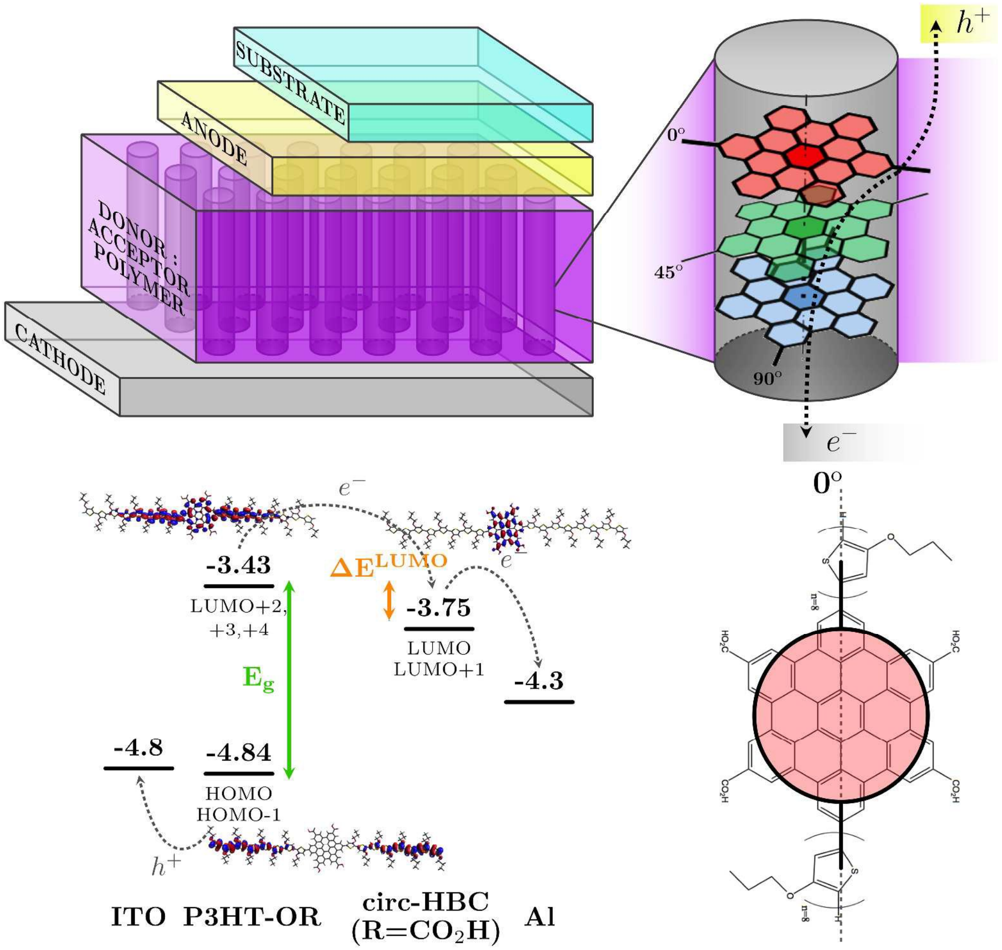

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