Modification of Anthraquinones to Optimize Singlet Fission Behavior

Petrenko D.V. & Silva R.T.

Department of Gastroenterology, Kherson Medical University, Kherson, Ukraine

Department of Digestive Medicine, Braga Clinical Academy, Braga, Portugal

Abstract

In this work, theoretical methods of quantum chemistry are employed to estimate the effects that the structural modification of 1,5- and 9,10-anthraquinone molecules might produce into their electronic structure, in the pursuit of a common strategy to improve the electrochemical and singlet fission features of conjugated quinones. The proposed modifications are the following: i) substitution of the carbonyl oxygen atom, ii) insertion of heteroatoms in the carbon backbone, and iii) introduction of electro-withdrawing and electro-donating substituents in different positions of the rings. This work shows how specific modifications of the electronic structure can be used to tune the electrochemistry and photophysics of the quinones, improving their suitability to be singlet fission sensitizers and cathode materials. As it was previously known, intermediate diradical characters favor the accomplishment of the singlet fission process. This can be achieved for 1,5-anthraquinone by introduction of B and Si atoms and electron donating groups in low spin density positions of the carbon backbone or N atoms in high spin density positions. The introduction of heteroatoms or substituents in 9,10-anthraquinone hardly facilitates the singlet fission process. Regarding the electrochemistry, it is observed that the reduction potentials greatly depend on the nature of the modification rather than on the diradical character.

Keywords: Singlet diradicals; quinones; reduction potentials, organic battery, redox, SF-DFT; excited states; singlet fission

1. INTRODUCTION

After some decades of development of the chemistry of open-shell diradical structures,[1,2] several investigations have been focused on how certain chemical modifications could affect the electronic structure and nature of the ground state of a given molecule. Although the extent of diradical character cannot be directly measured, it is often linked to the energy gap between the lowest spin triplet and singlet states, with smaller singlet-triplet splittings suggesting larger diradical characters. Localized singlet 1,3-diradicals were used by several authors[3,4,5] to rationalize the changes observed in the singlet-triplet energy splitting when electron-withdrawing (EWG) or electron-donating (EDG) groups are included into the main moiety. Similar studies including heteroatoms such as silicon[6,7] or nitrogen[8] are also available. It was concluded that both the heteroatoms and EWGs seemed to favor a singlet ground state. Heteroatoms have also been included into acene moieties in order to tune the diradical character and related properties.[9,10] Concretely, nitrogen atoms enhance the singlet-triplet splitting (and reduce the diradical character), while the number and exact position of these atoms could also determine the nature of the molecular ground state. The separation between singlet and triplet states has been also tuned using *meta*-benzoquinone, a non-Kekulé delocalized diradical, in which the oxygen atoms were substituted by CH_2,$C(NH_2)_2$ or $C(Ph)_2$ (Schlenk diradical), among others.[11,12,13] The latter, which shows a triplet ground state, was used to elucidate how EWG and EDG substituents may affect the nature of the ground state, considering the inductive and mesomeric effects (I and M, following Ingold's notation). In this sense, substituents with -M and -I effects reduce the singlet-triplet gap, while +M and +I substituents generate the opposite effect. This behavior was explained by means of the spin density. On the other hand, very little work can be found dealing with Kekulé delocalized diradicals, and theoretical analysis of their diradical character is rather scarce.[14,15,16,17,18] For example, Canesi and collaborators observed that the diradical character of a bithiophene derivative could be removed introducing alkoxy groups (EDG) on the structures.[19]

Since the diradical character of a molecule can be related to relative energies of low-lying states, it might be used to rationalize or even tune photophysical processes. In this sense, the diradical nature of organic chromophores has been related to its potential capacity to experience singlet fission,[20,21,22,23,24] and molecules with an intermediate diradical character (diradicaloids) have been proposed as one of the main classes of promising singlet fission sensitizers.[25,26,27,28,29,30] This spin-

allowed photophysical process allows one singlet excited state to be split into two triplet states, generating two low-energy excitons per absorbed photon. This has been proposed for organic photovoltaics, as it could enhance the efficiency reached by silicon[31,32] single-junction solar cells. One of the conditions that a sensitizer should fulfill is that the energy of the first singlet state should be equal or slightly higher than twice the energy of the first triplet, so that the process is kinetically and thermodynamically favored. Several studies have explored the impact of chemical substitution on potential singlet fission chromophores. For instance, it was found that the substitution of silicon atoms into an acene moiety leads to the diminution of the singlet-triplet gap,[33,34] reducing the value of the mentioned energy difference. The opposite behavior was observed when sp^2-conjugated nitrogen atoms were inserted into the backbone of the acene molecule.[35] The effect of the heteroatom strongly depends on the substitution site. Recent computational studies have shown how EWG groups slightly shift the previously mentioned condition to more negative values, especially for CN or NO_2 substituents.[36,37] Besides, other general requirements for solar cells such as good light-harvesting capability, photo-stability, production of triplets with a quantum yield around 200% or triplets near the energy gap of the semiconductor (E_g = 1.1 eV for Si) should also be considered and, thus, the list of conditions has limited considerably the number of efficient singlet fission sensitizers. The archetype molecules are tetracene,[38] pentacene[39,40,41] and hexacene,[42] however, those molecules lack the required stability for practical applications.

Another application where the modification of the diradical character may be relevant is the electrochemistry of molecules. Thus, substituted quinones[43,44,45] are considered very promising molecules for energy storage devices due to their unique properties, such as high energy density, flexibility, processability, sustainability and structural diversity.[44] For practical use in a battery, there must be a voltage gap large enough between a cathode with higher redox potential and an anode with lower redox potential. Nowadays, the highest average potential that can be obtained using carbonyl-based cells is around 2.8 V[46] (vs Li/Li^+ electrode), still far from common inorganic cathode materials (3.5 - 4 V). Thus, in the pursuit of higher energy density, understanding carbonyl utilization and predictable engineering of the reduction potentials is desired. Some relationships between redox voltage and properties such as electrophilicity and LUMO energy levels have already been established from theoretical studies.[14,15,47,48,49,50] Thus, it is well defined both experimentally and theoretically how the addition of EWGs or the substitution of nitrogen leads to the

enhancement of the reduction potentials, as shown by Hernández-Burgos et al.[51] Nevertheless, we are still far from the degree of understanding regarding the relation between electronic structure (diradical character) and redox activity that may be useful for a theoretically-aided selection prior to experimental characterization. Recently, the open-shell character and its relationship with the redox features of a set of quinones has been computationally investigated.[52]

In summary, the effect that chemical modifications might introduce in the diradical character of a molecule has been highlighted, yet it has not been completely unveiled. In this work, we have chosen two representative quinones, namely 1,5- and 9,10-anthraquinone, and performed a systematic study in order to rationalize the variation of the diradical character after chemical modification, as well as the redox potentials and low-lying excited states, in the pursuit of a common strategy to improve the electrochemical and singlet fission features of conjugated quinones. The proposed structural modifications are the following: i) substitution of the oxygen of the carbonyl group, ii) inclusion of heteroatoms in the aromatic rings, and iii) addition of substituents in different positions of the rings. For the sake of comparison, five experimentally known quinones structurally related to the 1,5-anthraquinone have been also included in the study. Finally, in addition to tuning the diradical character, some of the mentioned chemical modifications may be also useful to stabilize these molecules that otherwise may be difficult to synthesize. For instance, tetracyanoquinone dimethane derivatives[53,54] are good examples of stable *para*-substituted quinones, where the introduction of the cyano group in the terminal methylene blocks the reactive sites and delocalizes the spin density.

2. COMPUTATIONAL DETAILS

All geometry optimizations have been performed in gas phase within Density Functional Theory (DFT)[55,56] using the B3PW91 functional[57,58,59] in combination with the 6-31+G(d) basis set.[60] Harmonic vibrational frequencies were obtained at the same level of theory to confirm that all the structures were minima in the potential energy surfaces (no imaginary frequencies were found), to evaluate the zero-point vibrational energy (ZPVE) and the thermal corrections to the Gibbs free energy (T = 298 K, 1 atm) in the harmonic oscillator approximation. Single point calculations using the 6-311++G(d,p) basis set[61] were carried out on the optimized structures to refine the electronic energy for both the neutral, anionic and dianionic molecules.

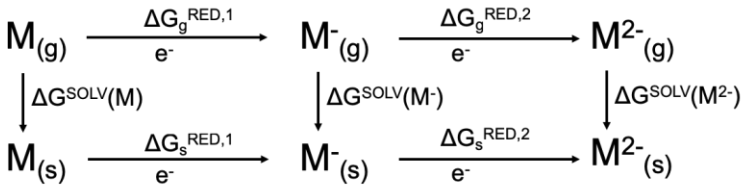

Figure 1. Thermodynamic cycle used in the calculation of the first (E_R^1) and second (E_R^2) redox potentials.

The reduction potentials have been calculated using the thermodynamic cycle shown in **Figure 1**, where the Gibbs free energy of the reduction half-reaction, ΔG_s^{RED}, consists of the free energy change in the gas phase and the solvation free energies (in acetonitrile) of the oxidized and reduced species:

$$\Delta G_s^{RED} = \Delta G_g^{RED} + \Delta G^{SOLV}(M^-) - \Delta G^{SOLV}(M)$$

The relation between the Gibbs energy and the electrode potential (E) of a half-cell is:

$$E = -\frac{\Delta G}{nF} - E_{ref}$$

where *F* is the Faraday constant (96485 C/mol) and *n* is the number of electrons in the half-reaction, with the subtraction of the reduction potential of the reference electrode. In this work, we have used the reference value -1.24 V, which represents the difference between the standard hydrogen electrode (SHE, -4.28 V)[62] and the Li/Li^+ redox couple (-3.04 V). In order to compare with the available experimental results, the following reference values have also been used: -4.67 V (saturated calomel electrode, SCE[63]), -4.988 V (ferrocene electrode[64]) and -4.305 V (silver electrode[65,66]).

The singlet diradical character is estimated from the spin-projected unrestricted Hartree-Fock (PUHF) theory,[67,68,69] using the the 6-311++G(d,p) basis set, as:

$$y_i = 1 - \frac{2T_i}{1 + T_i^2}$$

where T_i is defined as the orbital overlap and is calculated using the occupation number (*n*) of the UHF natural orbitals:

$$T_i = \frac{n_{HONO-i} - n_{LUNO+i}}{2}$$

Thus, from these equations both the diradical (y_0) and tetraradical (y_1) character can be estimated. An index value of 1 states for a perfect diradical (or tetraradical), while $y_0 = 0$ implies a closed-shell singlet (no tetraradical character). All these calculations have been carried out using the Gaussian 16 package.[70]

Finally, in order to describe the non-dynamic correlation effects in the calculation of the excited states, spin-flip DFT (SF-DFT)[71] calculations have been carried out with the BHandHLYP[72,73] functional and the 6-31G+(d,p) basis set, using the Q-Chem package.[74] This methodology has been proven to describe in a uniform way the three states of interest, namely, S_0, S_1 and T_1 (with $m_s = 0$), improving the representation provided by the broken-symmetry approximation.[75] To complement the diradical character analysis we have also estimated the number of unpaired electrons of the SF-BHandHLYP ground state by means of the (non-linear) Head-Gordon index:[76,77]

$$N_u = \sum_i n_i^2 \, (2 - n_i)^2$$

where n_i is the natural orbital occupation number.

3. RESULTS AND DISCUSSION

In this work, the conjugated carbonyls 1,5- and 9,10-anthraquinone, denoted as 1,5-AQ and 9,10-AQ, have been used to introduce different structural modifications, using the notation shown in **Figure 2** to label the carbon sites. Note that in 9,10-AQ the positions α and δ, as well as β and γ, are equivalent due to the symmetry of the molecule. First of all, the oxygen atoms of the carbonyl groups have been replaced by other atoms from periods 1, 2 and 3 of the periodic table, and saturated with hydrogen when required (S, Se, NH, PH, CH_2, SiH_2) as well as the $C(CN)_2$ substituent. Following, N, B, P and Si atoms have been introduced in α, β, γ and δ positions. Finally, two EWG (CF_3 and CN) and two EDG (OH and NH_2) groups were added in the same positions. In summary, 40 derivatives of 1,5-AQ and 24 of 9,10-AQ have been designed in order to elucidate the response that those variations might introduce in the diradical character, the reduction potentials and in the fulfillment of the singlet fission conditions.

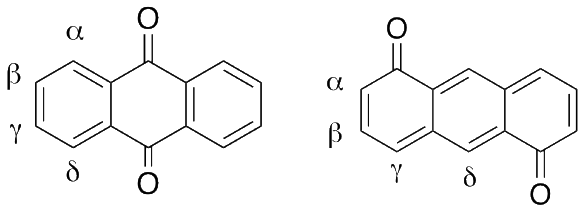

Figure 2. Molecular structure of 9,10-AQ (left) and 1,5-AQ (right), labeled with the four different positions where the chemical modifications are introduced.

3.1. Diradical character

As it was observed in previous works, many conjugated quinones show non-negligible diradical character and the ground state should be represented as a singlet open-shell state.[29,52] Thus, 9,10-AQ is a closed-shell molecule (y_0 = 0.00, N_u = 0.01), while 1,5-AQ presents a remarkable diradical character (y_0 = 0.60, N_u = 0.40). This feature is ascribed to the relative position of the carbonyl groups and may be explained using the resonant structures. Thus, the strong diradical character shown by 1,5-AQ is favored by the stabilization of a resonant structure that contains a π-electron system[78] (see **Figure 3**), while in 9,10-AQ two π-electron systems are already present in the closed-shell representation that would otherwise disappear in other resonant structure.

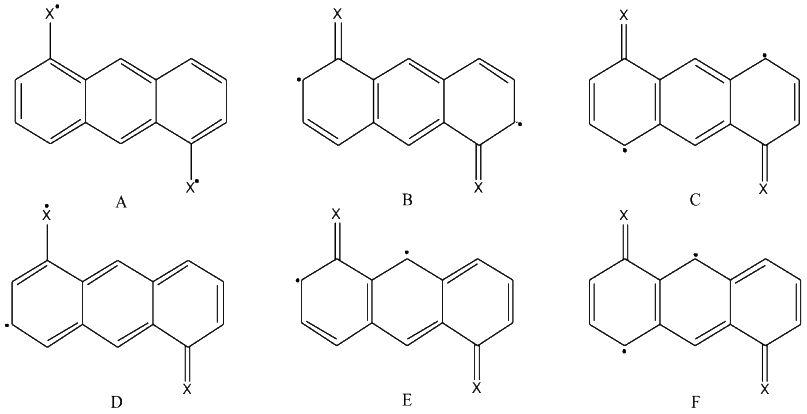

Figure 3. Selected resonance structures of the 1,5-AQ molecule.

The diradical character (y_0) of all the molecules considered in this work is represented in **Figure 4**. The numerical values of y_0 and N_u can be found in **Table 1, Table 2** and **Table 3**. In general, both y_0 and N_u show the same trends (see **Figure 5**). Regarding the substitution of the carbonyl oxygen, it is observed that all the 1,5-AQ derivatives show large diradical character (y_0 > 0.60), excepting when the carbonyl oxygen is substituted by S and Se, for which y_0 vanishes. Nevertheless, N_u

index clearly predicts larger diradical character than for the carbonyl, in agreement with the results observed in CASSCF calculations. This means that, in these two cases, the analysis via the PUHF solution is not able to properly capture the diradical character. Within periods 1 and 2, y_0 is reduced by increasing the atomic number: CH_2 > NH > O and SiH_2 > PH > S, while the variation within each group shows a general increase with the atomic number: CH_2 < SiH_2 and NH < PH, except for group 16. For 9,10-AQ, small enhancements of the diradical character are observed, from y_0 = 0.00 to y_0 = 0.07, 0.08 and 0.20 for CH_2, NH and PH, respectively.

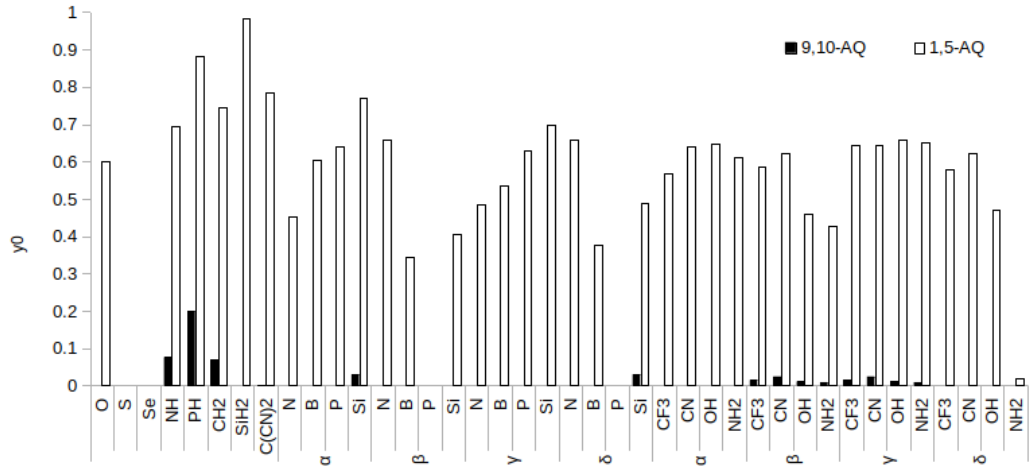

Figure 4. Diradical character (y_0) of the 9,10-AQ (black bars) and 1,5-AQ (white bars) derivatives.

Regarding the insertion of heteroatoms in the aromatic rings, large differences are accounted for 1,5-AQ. In general, it is observed a decrease in y_0 with the substitution, although it is highly dependent on both the atom and the position. It is remarkable the case of P, in which the y_0 for β and δ isomers is completely vanished, while for α and γ is slightly increased with respect to the reference. This trend is also observed in Si and B, while for N the opposite effect is found. Note that the Pauling electronegativities follow the trend Si (1.90) < B (2.04) < P (2.19) < C (2.55) < N (3.04). This behavior can be explained using the distribution of the spin density in the carbon backbone and the resonance structures of 1,5-AQ, that are represented in **Figure 3**. It can be observed that structures A, B and C contain one Clar sextet and, therefore, are expected to be dominant in the representation of the molecule. Structures B and C correspond to localization of the spin density on α and γ positions. Thus, the substitution with B, P or Si in positions with high spin density (α and γ) leads to an enhancement of y_0, while a decrease is found in β or δ (low spin

density). For nitrogen, the opposite trend is observed instead; the nitrogen atom is more electronegative than the carbon, which may explain its deviation from the general trend. As a summary, the diradical character increases following N < B < C < P < Si in positions α and γ, while in positions β and δ the trend goes P << B < Si < C < N. For 9,10-AQ, it is observed that the closed-shell structure is preserved in all cases except for Si, which slightly increases y_0 in α (and δ) position.

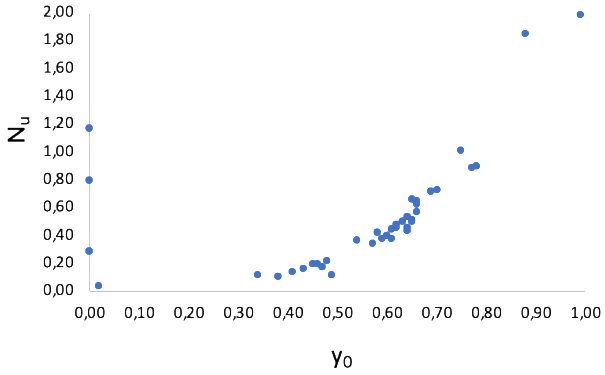

Figure 5. Relation between the diradical character (y_0) and the Head-Gordon index (N_u).

Table 1. Diradical character (y_0) and Head-Gordon index (N_u), low-lying excited states, E[S_1] (oscillator strength, *f*, in brackets) and E[T_1], and C1 condition, in eV, after substitution of the oxygen of the carbonyl group.

	9,10-Anthraquinone					1,5-Anthraquinone				
C=X	**y_0**	**N_u**	**E[S_1]**	**E[T_1]**	**C1**	**y_0**	**N_u**	**E[S_1]**	**E[T_1]**	**C1**
O	0.00	0.01	4.18 (0.00)	3.79	3.40	0.60	0.40	2.53 (0.95)	0.70	-1.14
S	0.00	0.00	2.06 (0.00)	1.88	1.71	0.00	0.80	1.89 (1.08)	0.36	-1.18
Se	0.00	0.00	1.53 (0.00)	1.69	1.84	0.00	1.17	1.69 (1.21)	0.20	-1.29
NH	0.08	0.05	5.09 (0.38)	3.46	1.82	0.69	0.72	2.39 (1.03)	0.48	-1.43
PH	0.20	0.09	3.40 (0.70)	1.94	0.48	0.88	1.85	2.51 (1.52)	0.05	-2.40
CH_2	0.07	0.04	4.67 (0.52)	3.24	1.81	0.75	1.01	2.42 (1.11)	0.31	-1.81
SiH_2	0.00	0.06	2.91 (0.76)	1.65	0.40	0.99	1.98	2.81 (2.10)	0.01	-2.79
$C(CN)_2$	0.00	0.03	3.79 (0.79)	2.83	1.87	0.78	0.90	1.80 (1.45)	0.28	-1.23

The introduction of CN, NH_2, OH and CH_3 substituents in 1,5-AQ produces small variations except for NH_2 and OH in β and δ positions. It is remarkable the value for NH_2 in δ position, which strongly decreases the diradical character (y_0 = 0.02). This behavior might be related to the existence of a hydrogen bond interaction

with the carbonyl oxygen, forming a stable six-membered ring and promoting the enol resonance form. This interaction is reflected in a longer C=O bond (0.04 Å), and a shorter C-NH_2 bond (0.01 Å), see Table S1 in the Supporting Information. On the other hand, the same interaction with the OH group is unstable and the migration of the hydrogen to the carbonyl takes place. Thus, we have only included the most stable isomer, with the hydroxyl H pointing to the opposite direction, which is 2.58 eV lower in energy.

Table 2. Diradical character (y_0) and Head-Gordon index (N_u), low-lying excited states, E[S_1] (oscillator strength, *f*, in brackets) and E[T_1], and C1 condition, in eV, after introduction of heteroatoms in the aromatic rings.

		9,10-Anthraquinone					1,5-Anthraquinone				
		y_0	N_u	E[S_1]	E[T_1]	C1	y_0	N_u	E[S_1]	E[T_1]	C1
α	N	0.00	0.01	4.35 (0.00)	3.93	3.52	0.45	0.19	2.88 (0.89)	1.13	-0.63
	B	0.00	0.00	3.58 (0.00)	3.13	2.69	0.61	0.38	2.45 (0.81)	0.60	-1.26
	P	0.00	0.01	4.01 (0.00)	3.30	2.59	0.64	0.53	2.26 (1.09)	0.54	-1.19
	Si	0.03	0.00	3.22 (0.00)	2.84	2.47	0.77	0.89	2.16 (1.33)	0.25	-1.65
β	N	0.00	0.00	3.67 (0.00)	4.73	5.79	0.66	0.57	2.62 (1.06)	0.54	-1.54
	B	0.00	0.00	3.58 (0.00)	3.17	2.76	0.34	0.12	2.51 (0.52)	1.25	-0.02
	P	0.00	0.01	3.79 (0.00)	3.26	2.72	0.00	0.29	2.49 (0.74)	1.02	-0.46
	Si	0.00	0.00	3.34 (0.00)	2.83	2.33	0.41	0.14	3.11 (0.43)	1.29	-0.54
γ	N	0.00	0.00	3.67 (0.00)	4.73	5.79	0.48	0.22	2.60 (0.76)	1.20	-0.20
	B	0.00	0.00	3.58 (0.00)	3.17	2.76	0.54	0.36	2.29 (0.97)	0.59	-1.12
	P	0.00	0.01	3.79 (0.00)	3.26	2.72	0.63	0.50	2.41 (1.03)	0.52	-1.37
	Si	0.00	0.00	3.34 (0.00)	2.83	2.33	0.70	0.73	2.13 (1.20)	0.31	-1.52
δ	N	0.00	0.01	4.35 (0.00)	3.93	3.52	0.66	0.65	2.56 (0.92)	0.51	-1.54
	B	0.00	0.00	3.58 (0.00)	3.13	2.69	0.38	0.10	2.67 (0.70)	1.48	0.29
	P	0.00	0.01	4.01 (0.00)	3.30	2.59	0.00	0.28	2.45 (0.76)	0.90	-0.65
	Si	0.03	0.00	3.22 (0.00)	2.84	2.47	0.49	0.11	2.36 (0.69)	1.34	0.31

For 1,9-AQ, the introduction of substituents in β position (and in γ) leads to a slight enhancement of y_0. In summary, the diradical character is mainly affected by the position of the substituent, while the nature (EWG or EDG) has smaller influence. This is a very relevant result from the experimental point of view, since some of the molecules proposed in this work may be difficult to synthesize, and chemical derivations may be needed in order to be isolated. With these results, we may conclude that the desired diradical character of the studied molecules will remain basically unchanged after substitution.

Table 3. Diradical character (y_0) and Head-Gordon index (N_u), low-lying excited states, E[S_1] (oscillator strength, *f*, in brackets) and E[T_1], and C1 condition, in eV, after introduction of substituents.

		9,10-Anthraquinone					1,5-Anthraquinone				
		y_0	N_u	E[S_1]	E[T_1]	C1	y_0	N_u	E[S_1]	E[T_1]	C1
α	CF_3	0.00	0.00	4.33 (0.00)	3.90	3.47	0.57	0.34	2.55 (1.03)	0.77	-1.01
	CN	0.00	0.01	4.42 (0.00)	3.84	3.26	0.64	0.43	2.33 (1.31)	0.63	-1.07
	OH	0.00	0.00	3.32 (0.40)	2.87	2.42	0.65	0.51	2.45 (1.06)	0.51	-1.44
	NH_2	0.00	0.00	3.04 (0.41)	2.62	2.20	0.61	0.44	2.40 (1.19)	0.52	-1.35
β	CF_3	0.01	0.01	4.28 (0.00)	3.82	3.36	0.59	0.38	2.61 (0.99)	0.75	-1.12
	CN	0.02	0.01	4.16 (0.00)	3.73	3.30	0.62	0.45	2.54 (1.00)	0.70	-1.15
	OH	0.01	0.00	3.69 (0.00)	3.28	2.88	0.46	0.19	2.56 (0.71)	1.07	-0.42
	NH_2	0.01	0.00	3.43 (0.00)	2.99	2.56	0.43	0.16	2.38 (0.49)	1.17	-0.03
γ	CF_3	0.01	0.01	4.28 (0.00)	3.82	3.36	0.65	0.50	2.40 (0.93)	0.61	-1.18
	CN	0.02	0.01	4.16 (0.00)	3.73	3.30	0.64	0.45	2.34 (0.98)	0.61	-1.12
	OH	0.01	0.00	3.69 (0.00)	3.28	2.88	0.66	0.62	2.42 (1.02)	0.44	-1.54
	NH_2	0.01	0.00	3.43 (0.00)	2.99	2.56	0.65	0.66	2.26 (0.95)	0.37	-1.53
δ	CF_3	0.00	0.00	4.33 (0.00)	3.90	2.62	0.58	0.42	2.63 (0.60)	0.73	-1.18
	CN	0.00	0.01	4.42 (0.00)	3.84	2.39	0.62	0.48	2.51 (0.83)	0.63	-1.25
	OH	0.00	0.00	3.32 (0.40)	2.87	1.79	0.47	0.17	2.65 (0.85)	1.22	-0.20
	NH_2	0.00	0.00	3.04 (0.42)	2.62	1.54	0.02	0.04	2.61 (0.61)	1.73	0.85

3.2. Singlet fission suitability

As it was mentioned in the Introduction, singlet fission chromophores have to fulfill two fundamental conditions, that will be referred as first (C1) and second conditions (C2), respectively:[20]

$$2E[T_1] - E[S_1] \leq 0$$

$$2E[T_1] - E[T_2] < 0$$

The C1 condition (first equation) states that twice the energy of the first triplet state (2E[T_1]) should be equal or slightly lower than the energy of the first singlet state (E[S_1]), in such a way that the process is thermally and kinetically favorable. Similarly, the C2 condition (second equation) states that 2E[T_1] must be lower in energy than the second triplet excited state (E[T_2]), in order to avoid decay into the triplet manifold.

The excitation energies E[S_1], E[T_1] and E[T_2] of the designed molecules have

been calculated to evaluate the C1 and C2 energetic requirements. In **Figure 7** is represented the C1 condition computed at the SF-BHandHLYP level, which has shown to perform very well for anthracene and also provides with very good S_1 values for tetracene and pentacene.[29] The numerical values are gathered in **Table 1**, **Table 2** and **Table 3**. Moreover, in order to mitigate the computational errors on the S_1 and T_1 energies, we compare C1 energies of the studied chromophores with those of tetracene (Tc) and pentacene (Pc) obtained at the same level of calculation. Tc and Pc are prototypical singlet fission materials presenting slightly endothermic and exothermic C1 energies, respectively.[20] Hence, in the following we consider potentially good singlet fission sensitizers those with C1 energies within the range stablished by these two reference chromophores as evaluated with SF-BHandHLYP (0.13 – 0.55 eV). Note that many of the computed E[S_1] states are dark (oscillator strength f = 0); nevertheless, the possibility to excite to a higher $S_0 \rightarrow S_n$ transition can be considered, E[S_n] in Tables S3 and S4, which may relax to the desired S_1 state. Excitation energies and singlet fission energetic condition C1 computed at different SF-DFT and TDDFT levels can be found as Supporting Information (Tables S2 – S4).

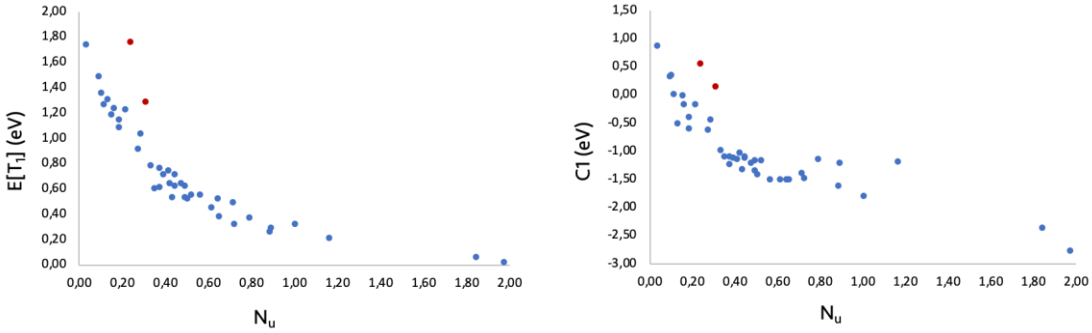

Figure 6. Relation between the lowest triplet excited state (E[T_1]), left, and the C1 energetic conditions, right (in eV) with the Head-Gordon index (N_u). Red points correspond to tetracene and pentacene.

Some general trends can be noted. For instance, general decrease of the energy of the first triplet excited state (E[T_1]) and the C1 condition with the diradical character (see **Figure 6**). Also, the 1,5-AQ derivatives show lower E[S_1] and E[T_1] values compared to the 9,10-AQ derivatives, in agreement with the larger diradical character observed. In a previous study,[29] we found that neither 1,5-AQ nor 9,10-AQ were potential candidates for singlet fission sensitizers, since the former shows a too exoergic (negative) C1 energy difference, while the latter a too endoergic (positive) one. Nevertheless, as shown in **Figure 7**, the substitution of the carbonyl oxygen in 9,10-AQ leads to a remarkable decrease of C1, in such a way that, in some cases (PH and SiH_2) these values fall within the range between tetracene and pentacene.

This means that these chemical modifications turn 9,10-AQ derivatives into potential singlet fission candidates. Inspecting the results for 1,5-AQ, we observe a shift to even more exoergic singlet fission (negative C1 values), a drawback for singlet fission.

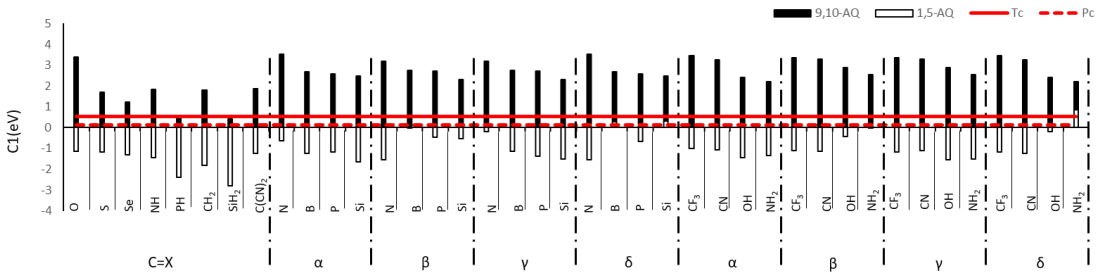

Figure 7. C1 condition of the 9,10-AQ (black bars) and 1,5-AQ (white bars) derivatives calculated with SF-DFT, in eV. Red dotted and straight lines stand for the C1 conditions of pentacene (Pc, 0.13 eV) and tetracene (Tc, 0.55 eV) respectively. Negative C1 values mean that the energy of S_1 is higher than twice the energy of T_1.

Considering the insertion of heteroatoms in the carbon backbone of 1,5-AQ, we find a general shift to less negative values of C1, especially for B and Si in β or δ positions and P (β) and N (γ), which reduce the large exoergicity observed in the unsubstituted AQ. On the contrary, B (α), P and Si (α and γ) and N (β and δ) induce slightly more negative C1 values. Two molecules of this group can be highlighted, with C1 conditions within the limits of Tc and Pc: derivatives with B and Si in δ position. It is remarkable how the molecules with B or Si in δ position greatly modify the exoergicity in C1, from the original -1.14 eV value of 1,5-AQ to ~0.3 eV. Thus, this can be an option to improve the singlet fission process, with minimum energy losses. It is also worth mentioning the B (β) and N (γ) substitutions results to C1 energies rather close to the Pc value. In the case of 9,10-AQ, C1 is slightly shifted to less positive values, and only N atom in α and δ positions slightly increases this value. This might help in the accomplishment of a singlet fission process, although only the derivatives with Si in α and δ positions get values closer to that of Pc.

The incorporation of EWG groups in 1,5-AQ induces little effect in C1, independently of the position. An increasing trend in C1 (shift to less negative values) is found for EDG groups, especially in β or δ positions, in such a way that NH_2 in β has a C1 value close to the Pc limit. Furthermore, this group in δ position (favoring a hydrogen bond with the carbonyl) produces such a positive shift that actually has and endoergic value (above the Tc value). On the other hand, in general 9,10-AQ

derivatives show less positive C1 values, in particular those derivatives with EDG groups, with the exception of CF_3 group, which is the only one to yield virtually the same C1 value as in the pristine 9,10-AQ. Nevertheless, all of these molecules still have too positive C1 values to be considered as potential candidates.

3.3. Electrochemistry

In general, the redox potentials of the1,5-AQ derivatives are higher (around 0.7 eV) than those of 9,10-AQ derivatives. This is in agreement with the fact that, in general, larger y_0 values accomplish larger redox potentials in the same family of molecules, such as the anthraquinones, although a general trend is difficult to devise.[52] It is important to remark that an accurate representation of solvent effects is mandatory for a proper calculation of redox potentials, especially in molecules such as anthraquinones, which may establish hydrogen bonds with protic solvents. In such a case, it has been observed that solvent molecules must be included explicitly in the calculation to obtain reliable results.[79] Nevertheless, for aprotic solvents, the use of the polarizable continuum model (PCM)[80,81,82,83] has been found to be very accurate for the first reduction potential, although the second reduction potentials show somewhat poorer accuracy.[79] In this work, we have chosen acetonitrile as a solvent represented by the PCM model, since most of the experimental works are performed in this solvent. Besides, in order to estimate the effect of the solvent in the redox features, we have also carried out the same calculations in chloroform (see Table S5). It is observed that the polarity of the solvent affects the redox potentials, which are decreased in a less polar solvent, such as chloroform.

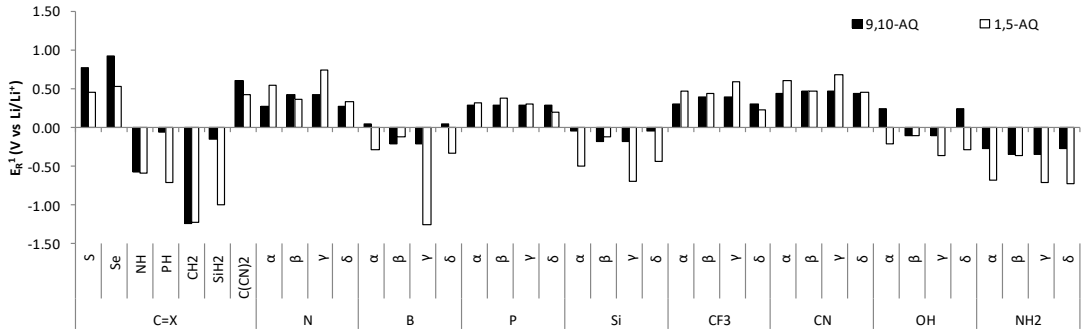

Figure 8. Difference between the first reduction potential of the studied molecules with respect to 1,5-AQ (white bars) and 9,10-AQ (black bars), in V, vs Li/Li^+.

In **Figure 8** is represented the variation of the redox potential (E_R^1) with respect to the 9,10-AQ and 1,5-AQ molecules. The numerical values are collected in **Tables 4, 5** and **6**. The number of carbonyl groups defines the number of successive

reductions that a molecule may undergo. The ratio between the number of electrons transferred and the mass of the molecule is known as the theoretical capacity (C_{THEO}). The product of the theoretical capacity and the reduction potential for the correspondent bielectronic process leads to the energy density (E_{DEN}), measured in $Whkg^{-1}$.

It is observed that the substitution of the carbonyl oxygen by S, Se and $C(CN)_2$ leads to an increase of E_R^1 (up to 3.80 V in the case of the 1,5-seleno-anthraquinone), while the lowest values are found for group 14 (1.23 V on the 9,10-anthraquinone dimethide), see **Table 4**. Similarly, E_{DEN} reaches its maximum for the S-, O- and $C(CN)_2$-containing molecules. The latter must be highlighted, as this substituent can be used to stabilize open-shell structures.[53,54]

Table 4. Diradical character (y_0) and Head-Gordon index (N_u), first and second reduction potentials (E_R^1 and E_R^2), in V vs Li/Li^+, and energy density (E_{DEN}), in Wh/kg, after the substitution of the oxygen of the carbonyl group. Experimental values in brackets.[84]

	9,10-Anthraquinone					1,5-Anthraquinone				
C=X	**y_0**	**N_u**	**E_R^1**	**E_R^2**	**E_{DEN}**	**y_0**	**N_u**	**E_R^1**	**E_R^2**	**E_{DEN}**
O	0.00	0.01	2.48 (2.26)	1.60 (1.86)	525	0.60	0.40	3.27	2.55	750
S	0.00	0.00	3.24	2.62	654	0.00	0.80	3.73	3.12	764
Se	0.00	0.00	3.40	2.86	502	0.00	1.17	3.80	3.26	566
NH	0.08	0.05	1.90	1.09	388	0.69	0.72	2.68	2.07	618
PH	0.20	0.09	2.42	1.89	481	0.88	1.85	2.57	2.43	558
CH_2	0.07	0.04	1.23	0.60	240	0.75	1.01	2.05	1.50	467
SiH_2	0.00	0.06	2.33	2.53	550	0.99	1.98	2.28	2.84	580
$C(CN)_2$	0.00	0.03	3.08 (2.85)	3.05	540	0.78	0.90	3.69	3.23	610

Regarding the introduction of heteroatoms, the N- and P-containing molecules show enhanced redox potentials, while these quantities are reduced in most of cases if B or Si atoms are inserted. This suggests that the nature of the heteroatom influences to a greater extent the redox features rather than the diradical character. Nevertheless, a trend is also observed for these features, for the 1,5-derivatives, that shows that in α and γ positions the variations are larger than in β or δ, in agreement with the trend observed for the diradical character. To illustrate this, the E_R^1 of the molecule containing a nitrogen in α and γ position grows 0.55 V and 0.74 V, respectively, with respect to the reference molecule. On the other hand, the introduction of N in β or δ positions results in an enhancement of only 0.37 and 0.33

V. This trend is not clearly observed with P, but the substitution of B in γ results in the reduction of E_R^1 more than 1 V, while in α is only 0.28 V. Finally, Si reduces E_R^1 around half a volt in α, γ and δ positions. The 9,10-derivatives also show higher redox potentials for N and P than for B and Si, while there are lower differences between the α and β positions than in the previous case.

The E_{DEN} of molecules with Si and P is lower than that of the original molecule, despite the P atom enhances the reduction potential. In the same way, boron induces higher C_{THEO} but lower E_R^1, so that E_{DEN} is reduced, except in case of the α-substituted isomer (for both 1,5 and 9,10 derivatives), that reaches higher E_R^1. In fact, in this case $E_R^2 > E_R^1$, which represents an odd behavior. Besides, the only molecules with a positive variation of E_{DEN} are those containing N atom, especially when is placed in α and γ.

Table 5. Diradical character (y_0) and Head-Gordon index (N_u), first and second reduction potentials (E_R^1 and E_R^2), in V vs Li/Li^+, and energy density (E_{DEN}), in Wh/kg, after the introduction of heteroatoms. Experimental values in brackets.[85]

		9,10-Anthraquinone					1,5-Anthraquinone				
		y_0	N_u	E_R^1	E_R^2	E_{DEN}	y_0	N_u	E_R^1	E_R^2	E_{DEN}
α	N	0.00	0.01	2.75	1.81	581	0.45	0.19	3.82	3.12	886
	B	0.00	0.00	2.52	1.77	564	0.61	0.38	2.99	3.19	813
	P	0.00	0.01	2.77	1.94	518	0.64	0.53	3.58	3.00	722
	Si	0.03	0.00	2.44	1.74	465	0.77	0.89	2.78	2.57	597
β	N	0.00	0.00	2.91 (2.71)	1.96	621	0.66	0.57	3.64	2.90	834
	B	0.00	0.00	2.27	1.36	477	0.34	0.12	3.15	2.43	733
	P	0.00	0.01	2.77	1.95	518	0.00	0.29	3.64	2.98	727
	Si	0.00	0.00	2.30	1.40	412	0.41	0.14	3.15	2.56	637
γ	N	0.00	0.00	2.91 (2.71)	1.96	621	0.48	0.22	4.02	3.20	920
	B	0.00	0.00	2.27	1.36	477	0.54	0.36	2.02	1.56	470
	P	0.00	0.01	2.77	1.95	518	0.63	0.50	3.57	2.93	713
	Si	0.00	0.00	2.30	1.40	412	0.70	0.73	2.58	2.65	584
δ	N	0.00	0.01	2.75	1.81	581	0.66	0.65	3.60	2.89	828
	B	0.00	0.00	2.52	1.77	564	0.38	0.10	2.93	2.66	736
	P	0.00	0.01	2.77	1.94	518	0.00	0.28	3.47	2.76	684
	Si	0.03	0.00	2.44	1.74	465	0.49	0.11	2.83	2.20	561

As it was observed in the previous subsection, the nature of the substituent is

more important in the variation of the redox properties than their position in the ring, for both 1,5- and 9,10-based molecules (see **Figure 8**). The EWGs (CF_3 and CN) enhance the redox potential (E_R^1), while the opposite effect is accounted for EDGs.[51] The only exception is the 9,10-derivative substituted in α with OH, possibly due to the formation of a hydrogen bond.

Table 6. Diradical character (y_0) and Head-Gordon index (N_u), first and second reduction potentials (E_R^1 and E_R^2), in V vs Li/Li^+, and energy density (E_{DEN}), in Wh/kg, after the introduction of substituents. Experimental values in brackets.[86]

		9,10-Anthraquinone					1,5-Anthraquinone				
		y_0	N_u	E_R^1	E_R^2	E_{DEN}	y_0	N_u	E_R^1	E_R^2	E_{DEN}
α	CF_3	0.00	0.00	2.78	1.76	353	0.57	0.34	3.74	3.03	527
	CN	0.00	0.01	2.92	1.95	506	0.64	0.43	3.88	3.22	736
	OH	0.00	0.00	2.72 (2.30)	2.12 (2.00)	540	0.65	0.51	3.07	2.32	601
	NH_2	0.00	0.00	2.20	1.50	417	0.61	0.44	2.59	1.97	513
β	CF_3	0.01	0.01	2.87	1.92	373	0.59	0.38	3.72	2.98	521
	CN	0.02	0.01	2.95	2.04	518	0.62	0.45	3.75	3.01	701
	OH	0.01	0.00	2.37	1.49	430	0.46	0.19	3.17	2.49	631
	NH_2	0.01	0.00	2.13 (2.22)	1.39	397	0.43	0.16	2.91	2.29	586
γ	CF_3	0.01	0.01	2.87	1.92	373	0.65	0.50	3.87	3.10	542
	CN	0.02	0.01	2.95	2.04	518	0.64	0.45	3.95	3.21	743
	OH	0.01	0.00	2.37	1.49	430	0.66	0.62	2.92	2.31	583
	NH_2	0.01	0.00	2.13 (2.22)	1.39	397	0.65	0.66	2.56	2.01	515
δ	CF_3	0.00	0.00	2.78	1.76	353	0.58	0.42	3.50	2.71	484
	CN	0.00	0.01	2.92	1.95	506	0.62	0.48	3.72	2.98	696
	OH	0.00	0.00	2.72 (2.30)	2.12 (2.00)	540	0.47	0.17	2.99	2.24	583
	NH_2	0.00	0.00	2.20	1.50	417	0.02	0.04	2.54	1.92	502

The increase of the redox potentials with EWG substituents is not enough to compensate the reduction of C_{THEO}, reducing also the value of E_{DEN} (see **Table 6**). Thus, the only substituent capable to mantain E_{DEN} as high as that of the unsubstituted molecule is CN, while all the other substituents reduce the energy density more than 100 $Whkg^{-1}$. Nevertheless, those values are comparable to common $LiCoO_2$ batteries.

3.4. Experimentally known 1,5-AQ derivatives

9,10-AQ is a stable molecule that has been widely investigated. On the other

hand, 1,5-AQ is unstable and no experimental data can be found in the literature. However, similar compounds have been synthesized by Nishida et al,[87] in which some EWG and a larger backbone (pentacene) are used, keeping the 1,5-AQ basic structure (**Figure 9**). In this section, the low-lying excited states and the reduction potentials of these compounds are calculated, as well as their diradical character. The results are gathered in **Table 7**. In order to relieve the computational effort, both isopropyl in molecule **3** and hexyl groups in molecules **4** and **5,** have been substituted by methyl.

The diradical character is reduced in all molecules with respect to 1,5-AQ, nevertheless, all of them show large y_0 values (0.42 – 0.53), which means that is possible to synthesize stable molecules with strong diradical character.

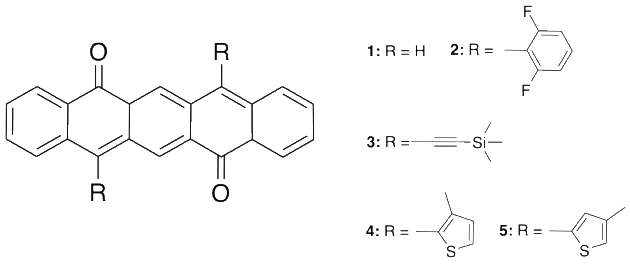

Figure 9. Experimentally synthesized molecular structures similar to 1,5-AQ.

The first reduction potential is increased in all cases and is slightly affected by the nature of the substituents. The theoretical energy densities are smaller due to the larger size of the molecules.

Table 7. Diradical character (y_0) and Head-Gordon index (N_u), first and second reduction potentials (E_R^1 and E_R^2), in V vs Li/Li$^+$, energy density (E_{DEN}), in Wh/kg, low lying excited states (E[S_1] and E[T_1]) and C1 condition, in eV. Experimental values in brackets.[87]

	y_0	N_u	E_R^1	E_R^2	E_{DEN}	E[S_1]	E[T_1]	C1
1,5-AQ	0.60	0.40	3.27	2.55	750	2.53	0.70	-1.14
1	0.42	0.13	2.83	2.15	433	2.70	1.20	-0.30
2	0.44	0.14	3.06 (3.15)	2.11 (2.61)	260	2.69 (2.15)	1.16	-0.38
3	0.53	0.18	3.04 (3.22)	2.25 (2.70)	283	2.38 (1.95)	0.89	-0.60
4	0.45	0.14	2.94 (3.12)	2.11 (2.60)	271	2.60 (2.07)	1.11	-0.37
5	0.45	0.13	3.06 (3.12)	2.07 (2.63)	274	2.56 (2.07)	1.10	-0.36

Regarding the excited states, the E[S_1] energy levels have been calculated to be around 0.5 eV higher than the experimental references, a difference that may be ascribed not only to the intrinsic error within SF-DFT, but also to the redshift of the

absorption maxima in solution with respect to the gas phase. $E[T_1]$ values are found a few tenths of an eV higher than the non-substituted 1,5-AQ molecule ($E[T_1]$ ~ 1 eV), which is related to the decrease in the diradical character. Moreover, the triplet energies are rather close to the energy gap in crystal silicon (1.1 eV). The obtained $2E[T_1] - E[S_1]$ values (C1 energy) fluctuate between -0.6 and -0.3 eV, not far from the value for Pc and showing a promising trend compared to the bare 1,5-AQ (-1.14 eV).

5. CONCLUSIONS

In this work, two families of anthraquinones, 1,5-AQ and 9,10-AQ, have been selected to be systematically modified in the pursuit of a common strategy to improve the electrochemical and singlet fission features of conjugated quinones. The modifications introduced can be collected in three main groups: i) substitution of the oxygen atom, ii) inclusion of heteroatoms in the carbon backbone, and iii) introduction of EWG and EDG substituents. In that manner, DFT and SF-DFT methodologies were employed to estimate the effect that those structural modifications might introduce on their low-lying excited states as well as in their redox potentials.

It is remarkable the large enhancement of the diradical character upon the substitution of the carbonyl oxygen by NH, PH, CH_2, SiH_2 or $C(CN)_2$. At the same time, the introduction of heteroatoms along the carbon moiety results on high dependence of the diradical character with the position of the modifications. In general, B, P and Si yield high diradical character in 1,5-AQ, in positions α and γ (high spin density), and low y_0 in positions β and δ (low spin density), while N shows the opposite effect.

As higher diradical characters shift the $2E[T_1] - E[S_1]$ energy difference to more negative values, some molecules are found to be appropriated for an efficient singlet fission process. In that manner, the substitution of oxygen by PH and SiH_2 on 9,10-AQ produces derivatives that might fulfill the C1 condition. The introduction of heteroatoms or substituents in 9,10-AQ cannot shift the C1 enough to reach an isoergic process, and only derivatives with Si (α, δ) get values closer to that of pentacene. However, these modifications in 1,5-AQ yield five more molecules with C1 similar to that of the tetracene and pentacene. For instance, the introduction of B (β, δ), N (γ) or Si (δ) might facilitate the accomplishment of the singlet fission process, as a consequence of a reduction of y_0. Also, an increasing trend in C1 is observed for EDG in 1,5-AQ, especially in β and δ positions, getting closer to the Pc limit.

The reduction potentials greatly depend on the nature of the modification, instead of the y_0. The substitution of the oxygen by S and Se largely enhances the reduction potentials, as well as the heterosubstitution of N and P or the introduction of EWG substituents, independently of the site. However, those modifications enhance the mass of the molecule, hence reducing E_{DEN}. Thus, it is recommended the introduction of N and the substituent CN, as they maintain quite large E_{DEN} values.

Finally, a set of five experimentally synthesized molecules closely related to 1,5-AQ have also been analyzed. The first reduction potentials are very accurately calculated, while the second reduction potential is slightly underestimated. An increase in E_R[1] is observed with respect to 1,5-AQ, nevertheless, lower energy densities are calculated. The calculated first singlet excited states overestimate the experimental data, as the calculations have been performed in gas phase and a redshift of the absorption maxima in solution with respect to the gas phase is expected. A shift to less exoergic C1 values is observed with respect to 1,5-AQ, suggesting a promising trend for the fulfillment of the singlet fission conditions and, therefore, they can be considered as promising candidates for this process.

ACKNOWLEDGEMENTS

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[1] Abe, M. *Chem. Rev.* **2007**, *113*, 7011-7088.

[2] Borden, W. T. In *The Foundations of Physical Organic Chemistry: Fifty Years of the James Flack Norris Award*; American Chemical Society, 2015; pp. 251-303.

[3] Conrad, M. P.; Pitzer, R. M.; Schaefer, H. F. *J. Am. Chem. Soc.* **1979,** *101*, 2245-2246

[4] Getty, S. J.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1521-1527.

[5] Xu, J. D.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 5425-5427.

[6] Ma, J.; Ding, Y.; Hattori, K.; Inagaki, S. *J. Org. Chem.* **2004**, *69*, 4245-4255.

[7] Abe, M.; Ishihara, C.; Tagegami, A. *J. Org. Chem.* **2004**, *69*, 7250-7255.

[8] Abe, M.; Kubo, E.; Nozaki, K.; Matsuo, T.; Hayashi, T. *Angew. Chem. Int. Ed.* **2006**, *45*, 7828-7831

[9] Amiri, S.; Schreiner, P. R. *J. Phys. Chem. A* **2009**, *113*, 11750-11757.

[10] Bunz, U. H. F. *Acc. Chem. Res.* **2015**, *48*, 1676-1686.

[11] Zhang, G.; Li, S.; Jiang, Y. *J. Phys. Chem. A* **2003**, *107*, 5573-5582.

[12] Fort, R. C.; Getty, S. J.; Hrovat, D. A.; Lahti, P. M.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 7549-7552.

[13] Latif, I. A.; Hansda, S.; Datta, S. N. *J. Phys. Chem. A* **2012**, *116*, 8599-8607.

[14] Bachman, J. E.; Curtiss, L. A.; Assary, R. S. *J. Phys. Chem. A* **2014**, *118*, 8852-8860.

[15] Er, S.; Suh, C.; Marshak, M. P.; Aspuru-Guzik, A. *Chem. Sci.* **2015**, *6*, 885-893.

[16] Nourmohammadian, F.; Yavari, I.; Mohtat, B.; Shafaei, S.Z. *Dyes Pigm.* **2007**, *75*, 479-482.

[17] Ohkita, M.; Sano, K.; Suzuki, T.; Tsuji, T.; Sato, T.; Niino, H. *Org. Biomol. Chem.* **2004**, *2*, 1044-1050.

[18] Golas, E.; Lewars, E.; F. Liebman, J. *J. Phys. Chem. A* **2009**, *113*, 9485-9500.

[19] Canesi, E. V.; Fazzi, D.; Colella, L.; Bertarelli, C.; Castiglioni, C. *J. Am. Chem. Soc.* **2012**, *134*, 19070-19083.

[20] Smith, M. B.; Michl, J. *Chem. Rev.* **2010**, *110*, 6891-6936.

[21] Casanova, D. *Chem. Rev.* **2018**, *118*, 7164-7207.

[22] Kim. H.; Zimmerman, P. M. *Phys. Chem. Chem. Phys.* **2018**, *20*, 30038-30094.

[23] Kim. H.; Keller, B.; Ho-Wu, R.; Abeyasinghe, N.; Vazquez, R. J.; Goodson, III, T.; Zimmerman, P. M. *J. Am. Chem. Soc.* **2018**, *140*, 7760-7763.

[24] Zimmerman, P. M.; Musgrave, C. B.; Head-Gordon, M. *Acc. Chem. Res.* **2013**, *46*, 1339-1347.

[25] Paci, I.; Johnson, J. C.; Chen, X.; Rana, G.; Popović, D.; David, D. E.; Nozik, A. J.; Ratner, M. A.; Michl, J. *J. Am. Chem. Soc.* **2006**, *128*, 16546-16553.

[26] Minami, T.; Nakano, M. *J. Phys. Chem. Lett.* **2011**, *3*, 145-150.

[27] Akdag, A.; Havlas, Z.; Michl, J. *J. Am. Chem. Soc.* **2012**, *134*, 14624-14631.

[28] Zimmerman, P. M.; Bell, F.; Casanova, D.; Head-Gordon, M. *J. Am. Chem. Soc.* **2011**, *133*, 19944-19952.

[29] López-Carballeira, D.; Casanova, D.; Ruipérez, F. *Phys. Chem. Chem. Phys.* **2017**, *19*, 30227-30238.

[30] Chien, A. D.; Molina, A. R.; Abeyasinghe, N.; Varnavski, O. P.; Goodson, III, T.; Zimmerman, P. M. *J. Phys. Chem. C* **2015**, *119*, 28258-28268

[31] Tayebjee, M. J. Y.; McCamey, D. R.; Schmidt, T. W. *J. Phys. Chem. Lett.* **2015**, *6*, 2367-2378.

[32] Hanna, M. C.; Nozik, A. J. *J. Appl. Phys.* **2006**, *100*, 074510.

[33] Bhattacharyya, K.; Pratik, S. M.; Datta, A. *J. Phys. Chem. C* **2015**, *119*, 25696-25702.

[34] Sardar, S. *J. Mol. Graph. Model.* **2017**, *74*, 24-37.

[35] Chen, Y.; Shen, L.; Li, X. *J. Phys. Chem. A* **2014**, *118*, 5700-5708.

[36] Shen, L.; Chen, Y.; Li, X.; Gao, J. *J. Mol. Graph. Model.* **2014**, *51*, 86-96.

[37] Shen, L.; Chen, Y.; Li, X.; Li, C. *J. Mol. Graph. Model.* **2016**, *66*, 187-195.

[38] Burdett, J. J.; Müller, A. M.; Gosztola, D.; Bardeen, C. J. *J. Chem. Phys.* **2010**, *133*, 144506.

[39] Lee, J.; Jadhav, P.; Baldo, M. A. *Appl. Phys. Lett.* **2009**, *95*, 33301.

[40] Rao, A.; Wilson, M. W. B.; Hodgkiss, J. M.; Albert-Seifried, S.; Bässler, H.; Friend, R. H. *J. Am. Chem. Soc.* **2010**, *132*, 12698-12703.

[41] Congreve, D. N.; Lee, J.; Thompson, N. J.; Hontz, E.; Yost, S. R.; Reusswig, P. D.; Bahlke, M. E.; Reineke, S.; Van Voorhis, T.; Baldo, M. A. *Science* **2013**, *340*, 334-337.

[42] Yost, S. R.; Lee, J.; Wilson, M. W.; Wu, T.; McMahon, D. P.; Parkhurst, R. R.; Thompson, N. J.; Congreve, D. N.; Rao, A.; Johnson, K.; Sfeir, M. Y.; Bawendi, M. G.; Swager, T. M.; Friend, R. H.; Baldo, M. A.; Van Voorhis, T. *Nat. Chem.* **2014**, *6*, 492-497

[43] Poizot, P.; Dolhem, F. *Energ. Environ. Sci.* **2011**, *4*, 2003.

[44] Song, Z.; Zhou, H. *Energ. Environ. Sci.* **2013**, *6*, 2280.

[45] Gracia, R.; Mecerreyes, D. *Polym. Chem.* **2013**, *4*, 2206.

[46] Genorio, B.; Pirnat, K.; Cerc-Korosec, R.; Dominko, R.; Gaberscek, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 7222-7224.

[47] Beheshti, A.; Norouzi, P.; Ganjali, M. R. *Int. J. Electrochem. Sci.* **2012**, *7*, 4811-4821.

[48] Yao, M.; Senoh, H.; Araki, M.; Sakai, T.; Tetsuo, S.; Yasuda, K. *ECS Trans.* **2010**, *28*, 3-10.

[49] Assary, R. S.; Brushett, F. R.; Curtiss, L. A. *RSC Adv.* **2014**, *4*, 57442-57451.

[50] Kim, K. C.; Liu, T.; Lee, S. W.; Jang, S. S. *J. Am. Chem. Soc.* **2016**, *138*, 2374-2382.

[51] Hernández-Burgos, K.; Burkhardt, S. E.; Rodríguez-Calero, G. G.; Hennig, R. G.; Abruña, H. D. *J. Phys. Chem. C* **2014**, *118*, 6046-6051.

[52] López-Carballeira, D.; Ruipérez, F. *Theor. Chem. Acc.* **2017**, *136*, 32.

[53] Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370-3374.

[54] Yanagimoto, T.; Takimiya, K.; Otsubo, T.; Ogura, F. *J. Chem. Soc. Chem. Comm.* **1993**, *6*, 519.

[55] Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964,** *136*, B864-B871.

[56] Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133-A1138.

[57] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3100.

[58] Perdew, J. P. In: *Electronic structure of solids '91*; Ziesche P.; Eschig H., Ed.; Akademie Verlag: Berlin, 1991; pp. 11-20.

[59] Burke K.; Perdew J. P.; Wang Y. In: *Electronic density functional theory: recent progess and new directions*; Dobson J. F.; Vignale G.; Das M. P., Eds.; Plenum: New York, 1998; pp. 81-121.

[60] Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257-2261.

[61] Dunning Jr., T. H. *J. Chem. Phys.* **1989**, *90*, 1007-1023.

[62] Isse, A. A.; Gennaro, A. *J. Phys. Chem. B* **2010**, *114*, 7894-7899.

[63] Namazian, M.; Coote, M. L. *J. Phys. Chem. A* **2007**, *111*, 7227-7232.

[64] Namazian, M.; Lin, C. Y.; Coote, M. L. *J. Chem. Theory Comput.* **2010**, *6*, 2721-2725.

[65] Popov, A. I.; Geske, D. H. *J. Am. Chem. Soc.* **1957**, *79*, 2074-2079.

[66] Kratochvil, B.; Lorah, E.; Garber, C. *Anal. Chem.* **1969**, *41*, 1793-1796.

[67] Yamanaka, S.; Kawamura, T.; Noro, T.; Yamaguchi, K. *J. Molec. Struct.* **1994**, *310*, 185-196.

[68] Nakano, M.; Kishi, R.; Nakagawa, N.; Ohta, S.; Takahashi, H.; Furukawa, S.; Kamada, K.; Ohta, K.; Champagne, B.; Botek, E.; Yamada, S.; Yamaguchi, K. *J. Phys. Chem. A* **2006**, *110*, 4238-4243.

[69] Nakano, M.; Kishi, R.; Ohta, S.; Takebe, A.; Takahashi, H.; Furukawa, S., Kubo, T.; Morita, Y.; Nakasuji, K.; Yamaguchi, K.; Kamada, K.; Ohta, K.; Champagne, B.; Botek, E. *J. Chem. Phys.* **2006**, *125*, 74113.

[70] Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

[71] Shao, Y.; Head-Gordon, M.; Krylov, A. I. *J. Chem. Phys.* **2003**, *118*, 4807-4818.

[72] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

[73] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.

[74] Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J.

Deng, X. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kuś, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. DiStasio, H. Do, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, Joseph Gomes, Magnus W.D. Hanson-Heine, Philipp H.P. Harbach, Andreas W. Hauser, Edward G. Hohenstein, Z. C. Holden, T.-C. Jagau, H. Ji, B.n Kaduk, K. Khistyaev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. D. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S.-P. Mao, N. Mardirossian, A. V. Marenich, Simon A. Maurer, Nicholas J. Mayhall, Eric Neuscamman, C. Melania Oana, Roberto Olivares-Amaya, Darragh P. O'Neill, J. A. Parkhill, T. M. Perrine, R. Peverati, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, S. M. Sharada, S. Sharma, D. W. Small, A. Sodt, T. Stein, D. Stück, Y.-C. Su, A. J. W. Thom, T. Tsuchimochi, V. Vanovschi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, J. Yang, S. Yeganeh, S. R. Yost, Z.-Q. You, I. Y. Zhang, X. Zhang, Y. Zhao, B. R. Brooks, G. K. L. Chan, D. M. Chipman, C. J. Cramer, W. A. Goddard, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. Schaefer, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xu, Alán Aspuru-Guzik, Roi Baer, Alexis T. Bell, Nicholas A. Besley, Jeng-Da Chai, Andreas Dreuw, Barry D. Dunietz, T. R. Furlani, S. R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D. S. Lambrecht, W. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. V. Voorhis, J. M. Herbert, A. I. Krylov, P. M.W. Gill, M. Head-Gordon, *Mol. Phys.* **2015**, *113*, 184-215.

[75] Bernard, Y. A.; Shao, Y.; Krylov, A. I. *J. Chem. Phys.* **2012**, *136*, 204103.

[76] Head-Gordon, M. *Chem. Phys. Lett.* **2003**, *327*, 508-511.

[77] Orms, N.; Rehn, D. R.; Dreuw, A.; Krylov, A. I. *J. Chem. Theory Comput.* **2018**, *14*, 638-648.

[78] Szatylowicz, H.; Krygowski, T. M.; Solà, M.; Palusiak, M.; Dominikowska, J.; Stasyuk, O. A.; Poater, J. *Theor. Chem. Acc.* **2015**, *134*, 35.

[79] Kim, H.; Goodson, III, T.; Zimmerman, P. M. *J. Phys. Chem. C* **2016**, *120*, 22235-22247.

[80] Cossi, M.; Barone, V.; Cammi, R. *Chem. Phys. Lett.* **1996**, *255*, 327-335.

[81] Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032-3041.

[82] Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210-3221.

[83] Barone, V.; Cossi, M.; Tomasi, J. *J. Comput. Chem.* **1998**, *19*, 404-417.

[84] Takeda, T.; Taniki, R.; Masuda, A.; Honma, I.; Akutagawa, T. *J. Power Sources* **2016**, *328*, 228-234.

[85] Liang, Y.; Zhang, P.; Yang, S.; Tao, Z.; Chen, J. *Adv. Energy Mater.* **2013**, *3*, 600-605.

[86] Zeng, R.; Xing, L.; Qiu, Y.; Wang, Y.; Huang, W.; Li, W.; Yang, S. *Electrochim. Acta* **2014**, *146*, 447-454.

[87] Nishida, J.; Fujiwara, Y.; Yamashita, Y. *Org. Lett.* **2009**, *11*, 1813-1816.