Supplementary Information for

Improvement of the electrochemical and singlet fission properties of anthraquinones by modification of the diradical character

Diego López-Carballeira[1], María Zubiria[2] David Casanova[2,3] and Fernando Ruipérez[1,*]

[1]POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 72, 20018 Donostia – San Sebastián, Spain

[2]Donostia International Physics Center (DIPC), 20018 Donostia, Euskadi, Spain

[3]IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Euskadi, Spain

Content:

Table S1: Selected bond distances, in Å, for derivatives of 1,5-AQ and 9,10-AQ that may establish intramolecular hydrogen bonds.

	1,5-AQ (α)		1,5-AQ (δ)		9,10-AQ (α)		9,10-AQ (β)	
	X=OH	X=NH_2	X=OH	X=NH_2	X=OH	X=NH_2	X=OH	X=NH_2
C=O	1.25	1.24	1.23	1.26	1.24	1.24	1.23	1.23
X-H	0.99	1.01	0.97	1.04	1.00	1.02	0.97	1.01
C-X	1.33	1.34	1.33	1.33	1.33	1.35	1.36	1.38
C=O - - H	1.97	2.18	--	1.63	1.67	1.85	--	--

Table S2. Diradical character (y_0) and Head-Gordon index (N_u), low-lying excited states, $E[S_1]$ and $E[T_1]$, and C1 condition, in eV, calculated by SF-DFT and using the $M_S = 1$ component of T_1.

		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	3.37	2.56	0.60	0.40	2.53	-0.01	-2.56
	S	0.00	0.00	2.06	1.53	1.01	0.00	0.80	1.89	-0.23	-2.36
	Se	0.00	0.00	1.53	1.08	0.63	0.00	1.17	1.69	-0.30	-2.21
	NH	0.08	0.05	5.09	3.80	2.91	0.69	0.72	2.39	-0.36	-3.10
	PH	0.20	0.09	3.40	1.58	-0.25	0.88	1.85	2.51	-0.52	-3.55
	CH_2	0.07	0.04	4.67	2.77	0.88	0.75	1.01	2.42	-0.51	-3.45
	SiH_2	0.00	0.06	2.91	1.39	-0.13	0.99	1.98	2.81	-0.41	-3.62
	$C(CN)_2$	0.00	0.03	3.79	2.39	0.99	0.78	0.90	1.80	-0.42	-2.63
α	**N**	0.00	0.01	4.35	3.49	2.64	0.45	0.19	2.88	0.48	-1.91
	B	0.00	0.00	3.58	2.83	2.09	0.61	0.38	2.45	0.02	-2.41
	P	0.00	0.01	4.01	2.81	2.16	0.64	0.53	2.26	-0.05	-2.37
	Si	0.03	0.00	3.22	2.58	1.94	0.77	0.89	2.16	-0.22	-2.59
β	**N**	0.00	0.00	3.67	2.98	2.30	0.66	0.57	2.62	-0.22	-3.06
	B	0.00	0.00	3.58	2.84	2.11	0.34	0.12	2.51	0.68	-1.15
	P	0.00	0.01	3.79	2.87	1.95	0.00	0.29	2.49	0.33	-1.84
	Si	0.00	0.00	3.34	2.52	1.70	0.41	0.14	3.11	0.72	-1.66
γ	**N**	0.00	0.00	3.67	2.98	2.30	0.48	0.22	2.60	0.44	-1.71
	B	0.00	0.00	3.58	2.84	2.11	0.54	0.36	2.29	0.09	-2.12
	P	0.00	0.01	3.79	2.87	1.95	0.63	0.50	2.41	0.08	-2.57
	Si	0.00	0.00	3.34	2.52	1.70	0.70	0.73	2.13	0.18	-2.49
δ	**N**	0.00	0.01	4.35	3.49	2.64	0.66	0.65	2.56	-0.28	-3.12
	B	0.00	0.00	3.58	2.83	2.09	0.38	0.10	2.67	0.89	-0.88
	P	0.00	0.01	4.01	2.81	2.16	0.00	0.28	2.45	0.23	-1.98
	Si	0.03	0.00	3.22	2.58	1.94	0.49	0.11	2.36	0.78	-0.80
α	**CF_3**	0.00	0.00	4.33	3.48	2.62	0.57	0.34	2.55	0.09	-2.37
	CN	0.00	0.01	4.42	3.40	2.39	0.64	0.43	2.33	-0.06	-2.45
	OH	0.00	0.00	3.32	2.55	1.79	0.65	0.51	2.45	-0.07	-2.60
	NH_2	0.00	0.00	3.04	2.29	1.54	0.61	0.44	2.40	0.04	-2.32
β	**CF_3**	0.01	0.01	4.28	3.40	2.52	0.59	0.38	2.61	0.02	-2.57
	CN	0.02	0.01	4.16	3.28	2.41	0.62	0.45	2.54	-0.06	-2.66
	OH	0.01	0.00	3.69	2.92	2.16	0.46	0.19	2.56	0.44	-1.68
	NH_2	0.01	0.00	3.43	2.65	1.88	0.43	0.16	2.38	0.57	-1.25
γ	**CF_3**	0.01	0.01	4.28	3.40	2.52	0.65	0.50	2.40	-0.16	-2.71
	CN	0.02	0.01	4.16	3.28	2.41	0.64	0.45	2.34	-0.16	-2.65
	OH	0.01	0.00	3.69	2.92	2.16	0.66	0.62	2.42	-0.20	-2.82
	NH_2	0.01	0.00	3.43	2.65	1.88	0.65	0.66	2.26	-0.17	-2.60
δ	**CF_3**	0.00	0.00	4.33	3.48	2.62	0.58	0.42	2.63	0.00	-2.63
	CN	0.00	0.01	4.42	3.40	2.39	0.62	0.48	2.51	-0.11	-2.72

OH	0.00	0.00	3.32	2.55	1.79	0.47	0.17	2.65	0.56	-1.52
NH_2	0.00	0.00	3.04	2.29	1.54	0.02	0.04	2.61	1.25	-0.11

Table S3. Diradical character (y_0) and Head-Gordon index (N_u), low-lying excited states, E[S_1], E[T_1] and E[S_n] (oscillator strength, *f*, in brackets), and C1 condition, in eV, and oscillator strength (*f)* calculated by TD-DFT using the B3PW91 functional.

		9,10-Anthraquinone						**1,5-Anthraquinone**					
	C=X	y_0	N_u	E[S_1]	E[T_1]	C1	E[S_n]	y_0	N_u	E[S_1]	E[T_1]	C1	E[S_n]
	O	0.00	0.01	2.93 (0.00)	2.50	2.09	3.91 (0.13)	0.60	0.40	1.95 (0.00)	0.43	-1.10	2.70 (0.90)
	S	0.00	0.00	1.56 (0.00)	1.19	0.81	---	0.00	0.80	0.91 (0.00)	0.10	-0.71	2.40 (1.04)
	Se	0.00	0.00	1.14 (0.00)	0.79	0.43	3.03 (0.10)	0.00	1.17	0.64 (0.00)	-0.07	-0.79	2.37 (1.21)
	NH	0.08	0.05	3.94 (0.01)	2.83	1.72	---	0.69	0.72	2.59 (1.02)	0.16	-2.27	---
	PH	0.20	0.09	3.10 (0.00)	1.57	0.05	---	0.88	1.85	1.83 (0.00)	-0.45	-2.73	2.44 (1.34)
	CH_2	0.07	0.04	3.99 (0.00)	2.62	1.25	---	0.75	1.01	-2.32 (0.00)	-0.06	2.21	2.47 (1.10)
	SiH_2	0.00	0.06	2.81 (0.01)	1.28	-0.25	---	0.99	1.98	1.56 (0.00)	-0.85	-3.25	2.60 (1.44)
	$C(CN)_2$	0.00	0.03	3.32 (0.00)	2.17	1.02	3.34 (0.03)	0.78	0.90	2.16 (0.00)	0.01	-2.13	3.49 (0.01)
α	**N**	0.00	0.01	2.85 (0.00)	2.40	1.95	3.61 (0.01)	0.45	0.19	1.74 (0.00)	0.81	-0.12	2.67 (0.01)
	B	0.00	0.00	2.94 (0.00)	2.36	1.78	3.28 (0.31)	0.61	0.38	2.13 (0.00)	0.42	-1.30	---
	P	0.00	0.01	2.57 (0.00)	2.21	1.85	3.41 (0.15)	0.64	0.53	1.53 (0.00)	0.32	-0.89	2.49 (1.09)
	Si	0.03	0.00	2.80 (0.00)	2.13	1.45	2.97 (0.13)	0.77	0.89	1.85 (0.00)	0.03	-1.79	---
β	**N**	0.00	0.00	2.61 (0.00)	2.27	1.92	3.41 (0.01)	0.66	0.57	1.42 (0.00)	0.26	-0.89	2.76 (0.96)
	B	0.00	0.00	3.11 (0.00)	2.55	2.00	3.36 (0.01)	0.34	0.12	2.23 (0.00)	0.91	-0.42	2.45 (0.45)
	P	0.00	0.01	2.82 (0.00)	2.42	2.03	3.62 (0.07)	0.00	0.29	1.75 (0.00)	0.67	-0.41	2.54 (0.74)
	Si	0.00	0.00	2.92 (0.00)	2.23	1.53	3.43 (0.13)	0.41	0.14	1.93 (0.00)	0.90	-0.13	2.30 (0.40)
γ	**N**	0.00	0.00	2.61 (0.00)	2.27	1.92	3.41 (0.01)	0.48	0.22	1.72 (0.00)	0.80	-0.12	2.42 (0.01)
	B	0.00	0.00	3.11 (0.00)	2.55	2.00	3.36 (0.01)	0.54	0.36	2.09 (0.00)	0.19	-1.72	---
	P	0.00	0.01	2.82 (0.00)	2.42	2.03	3.62 (0.07)	0.63	0.50	1.71 (0.00)	0.33	-1.06	2.55 (0.95)
	Si	0.00	0.00	2.92 (0.00)	2.23	1.53	3.43 (0.13)	0.70	0.73	2.28 (0.00)	0.05	-2.18	2.38 (1.18)
δ	**N**	0.00	0.01	2.85 (0.00)	2.40	1.95	3.61 (0.01)	0.66	0.65	1.50 (0.00)	0.21	-1.08	2.67 (0.84)
	B	0.00	0.00	2.94 (0.00)	2.36	1.78	3.28 (0.31)	0.38	0.10	2.05 (0.00)	1.13	0.22	2.60 (0.44)
	P	0.00	0.01	2.57 (0.00)	2.21	1.85	3.41 (0.15)	0.00	0.28	1.71 (0.00)	0.58	-0.55	---
	Si	0.03	0.00	2.80 (0.00)	2.13	1.45	2.97 (0.13)	0.49	0.11	2.09 (0.00)	0.94	-0.21	2.42 (0.59)
α	**CF_3**	0.00	0.00	2.96 (0.00)	2.51	2.06	---	0.57	0.34	1.93 (0.00)	0.49	-0.94	2.68 (1.00)
	CN	0.00	0.01	2.79 (0.00)	2.38	1.97	3.65 (0.15)	0.64	0.43	1.89 (0.00)	0.37	-1.16	2.52 (1.32)
	OH	0.00	0.00	3.04 (0.31)	2.24	1.43	---	0.65	0.51	2.40 (0.00)	0.33	-1.75	2.58 (0.85)
	NH_2	0.00	0.00	2.80 (0.32)	2.01	1.22	---	0.61	0.44	2.41 (0.00)	0.37	-1.67	2.50 (0.82)
β	**CF_3**	0.01	0.01	2.89 (0.00)	2.47	2.04	3.94 (0.14)	0.59	0.38	1.96 (0.00)	0.47	-1.02	2.72 (0.93)
	CN	0.02	0.01	2.88 (0.00)	2.45	2.03	3.81 (0.15)	0.62	0.45	1.87 (0.00)	0.41	-1.05	2.65 (0.96)
	OH	0.01	0.00	3.02 (0.00)	2.59	2.16	3.74 (0.16)	0.46	0.19	2.13 (0.00)	0.77	-0.59	2.62 (0.60)
	NH_2	0.01	0.00	2.97 (0.00)	2.31	1.64	3.29 (0.01)	0.43	0.16	2.11 (0.00)	0.84	-0.43	2.39 (0.33)
γ	**CF_3**	0.01	0.01	2.89 (0.00)	2.47	2.04	3.94 (0.14)	0.65	0.50	1.71 (0.00)	0.33	-1.06	2.62 (0.90)
	CN	0.02	0.01	2.88 (0.00)	2.45	2.03	3.81 (0.15)	0.64	0.45	1.74 (0.00)	0.34	-1.05	2.52 (0.95)
	OH	0.01	0.00	3.02 (0.00)	2.59	2.16	3.74 (0.16)	0.66	0.62	2.09 (0.00)	0.19	-1.72	2.57 (0.98)
	NH_2	0.01	0.00	2.97 (0.00)	2.31	1.64	3.29 (0.01)	0.65	0.66	2.27 (0.00)	0.13	-2.01	2.42 (0.94)
δ	**CF_3**	0.00	0.00	2.96 (0.00)	2.51	2.06	---	0.58	0.42	2.03 (0.00)	0.45	-1.13	2.12 (0.01)
	CN	0.00	0.01	2.79 (0.00)	2.38	1.97	3.65 (0.15)	0.62	0.48	1.77 (0.00)	0.36	-1.05	2.58 (0.75)
	OH	0.00	0.00	3.04 (0.31)	2.24	1.43	---	0.47	0.17	1.88 (0.00)	0.92	-0.04	2.75 (0.77)
	NH_2	0.00	0.00	2.80 (0.32)	2.01	1.22	---	0.02	0.04	2.56 (0.00)	1.36	0.16	2.65 (0.50)

Table S4. Diradical character (y_0) and Head-Gordon index (N_u), low-lying excited states, E[S_1], E[T_1] and E[S_n] (oscillator strength, *f*, in brackets), and C1 condition, in eV, and oscillator strength (*f)* calculated by TD-DFT using the M062X functional.

		9,10-Anthraquinone						1,5-Anthraquinone					
	C=X	y_0	N_u	E[S_1]	E[T_1]	C1	E[S_n]	y_0	N_u	E[S_1]	E[T_1]	C1	E[S_n]
	O	0.00	0.01	4.34 (0.00)	3.59	2.84	4.52 (0.15)	0.60	0.40	2.56 (0.00)	0.50	-1.57	2.63 (0.95)
	S	0.00	0.00	1.56 (0.01)	1.19	0.81	---	0.00	0.80	1.23 (0.00)	0.08	-1.07	2.21 (1.08)
	Se	0.00	0.00	1.33 (0.00)	1.01	0.68	3.31 (0.96)	0.00	1.17	0.89 (0.00)	-0.18	-1.23	2.12 (1.21)
	NH	0.08	0.05	4.28 (0.01)	3.23	2.19	---	0.69	0.72	2.59 (1.02)	0.16	-2.27	---
	PH	0.20	0.09	3.58 (0.70)	1.83	0.08	---	0.88	1.85	2.09 (0.00)	-0.59	-3.28	2.16 (1.52)
	CH_2	0.07	0.04	4.56 (0.01)	3.05	1.54	---	0.75	1.01	2.29 (1.11)	0.00	-2.28	---
	SiH_2	0.00	0.06	3.12 (0.76)	1.50	-0.13	---	0.99	1.98	1.72 (0.00)	-1.14	-4.01	2.34 (2.10)
	$C(CN)_2$	0.00	0.03	3.89 (0.00)	2.53	1.18	3.94 (0.79)	0.78	0.90	2.04 (.145)	-0.03	-2.09	---
α	**N**	0.00	0.01	3.16 (0.00)	2.74	2.31	4.29 (0.01)	0.45	0.19	2.32 (0.00)	0.98	-0.36	2.54 (0.01)
	B	0.00	0.00	3.16 (0.01)	2.73	2.30	---	0.61	0.38	2.29 (0.01)	0.55	-1.19	---
	P	0.00	0.01	2.92 (0.00)	2.58	2.23	3.33 (0.01)	0.64	0.53	1.53 (0.00)	0.32	-0.89	2.49 (1.09)
	Si	0.03	0.00	3.43 (0.42)	2.43	1.42	---	0.77	0.89	2.16 (1.33)	-0.14	-2.44	---
β	**N**	0.00	0.00	3.04 (0.00)	2.68	2.31	4.24 (0.01)	0.66	0.57	1.95 (0.00)	0.28	-1.39	2.65 (1.06)
	B	0.00	0.00	3.36 (0.00)	2.97	2.58	3.38 (0.01)	0.34	0.12	2.64 (0.52)	1.13	-0.38	---
	P	0.00	0.01	3.15 (0.00)	2.78	2.40	4.19 (0.10)	0.00	0.29	2.32 (0.00)	0.85	-0.62	2.44 (0.01)
	Si	0.00	0.00	3.47 (0.00)	2.53	1.59	3.96 (0.24)	0.41	0.14	2.52 (0.43)	1.14	-0.23	---
γ	**N**	0.00	0.00	3.04 (0.00)	2.68	2.31	4.24 (0.01)	0.48	0.22	2.38 (0.00)	1.01	-0.35	2.84 (0.76)
	B	0.00	0.00	3.36 (0.00)	2.97	2.58	3.38 (0.01)	0.54	0.36	1.74 (0.01)	0.38	-0.98	---
	P	0.00	0.01	3.15 (0.00)	2.78	2.40	4.19 (0.10)	0.63	0.50	2.48 (1.03)	0.31	-1.86	---
	Si	0.00	0.00	3.47 (0.00)	2.53	1.59	3.96 (0.24)	0.70	0.73	2.18 (1.20)	-0.06	-2.31	---
δ	**N**	0.00	0.01	3.16 (0.00)	2.74	2.31	4.29 (0.01)	0.66	0.65	2.03 (0.00)	0.24	-1.54	2.54 (0.92)
	B	0.00	0.00	3.16 (0.01)	2.73	2.30	---	0.38	0.10	2.38 (0.00)	1.33	-0.28	2.84 (070)
	P	0.00	0.01	2.92 (0.00)	2.58	2.23	3.33 (0.01)	0.00	0.28	2.32 (0.01)	0.73	-0.85	---
	Si	0.03	0.00	3.43 (0.42)	2.43	1.42	---	0.49	0.11	2.59 (0.68)	1.14	-0.29	---
α	**CF_3**	0.00	0.00	3.25 (0.01)	2.83	2.41	---	0.57	0.34	2.59 (0.00)	0.58	-1.42	2.63 (1.03)
	CN	0.00	0.01	3.11 (0.00)	2.72	2.33	4.35 (0.16)	0.64	0.43	2.44 (1.31)	0.42	-1.61	---
	OH	0.00	0.00	3.56 (0.40)	2.69	1.82	---	0.65	0.51	2.47 (1.06)	0.24	-2.00	---
	NH_2	0.00	0.00	3.29 (0.42)	2.44	1.59	---	0.61	0.44	2.39 (1.19)	0.27	-1.86	---
β	**CF_3**	0.01	0.01	4.43 (0.00)	3.47	2.51	4.56 (0.17)	0.59	0.38	2.57 (0.00)	0.56	-1.46	2.67 (0.99)
	CN	0.02	0.01	4.31 (0.00)	3.36	2.42	4.45 (0.18)	0.62	0.45	2.50 (0.00)	0.50	-1.51	2.59 (1.00)
	OH	0.01	0.00	3.84 (0.00)	3.09	2.33	4.37 (0.17)	0.46	0.19	2.72 (0.71)	0.93	-0.86	---
	NH_2	0.01	0.00	3.33 (0.00)	2.78	2.23	4.07 (0.28)	0.43	0.16	2.62 (0.49)	1.04	-0.55	---
γ	**CF_3**	0.01	0.01	4.43 (0.00)	3.47	2.51	4.56 (0.17)	0.65	0.50	2.36 (0.00)	0.39	-1.59	2.54 (0.94)
	CN	0.02	0.01	4.31 (0.00)	3.36	2.42	4.45 (0.18)	0.64	0.45	2.41 (0.00)	0.40	-1.61	2.46 (0.98)
	OH	0.01	0.00	3.84 (0.00)	3.09	2.33	4.37 (0.17)	0.66	0.62	2.40 (1.02)	0.13	-2.13	---
	NH_2	0.01	0.00	3.33 (0.00)	2.78	2.23	4.07 (0.28)	0.65	0.66	2.21 (0.95)	0.03	-2.16	---
δ	**CF_3**	0.00	0.00	3.25 (0.01)	2.83	2.41	---	0.58	0.42	2.57 (0.00)	0.55	-1.46	2.57 (0.60)
	CN	0.00	0.01	3.11 (0.00)	2.72	2.33	4.35 (0.16)	0.62	0.48	2.31 (0.00)	0.43	-1.44	2.53 (0.83)
	OH	0.00	0.00	3.56 (0.40)	2.69	1.82	---	0.47	0.17	2.58 (0.00)	1.09	-0.39	2.76 (0.01)
	NH_2	0.00	0.00	3.29 (0.42)	2.44	1.59	---	0.02	0.04	2.91 (0.61)	1.61	0.31	---

Table S5. First (E_R^1) and second (E_R^2) reduction potentials, in V, calculated in chloroform.

	9,10-Anthraquinone		1,5-Anthraquinone	
	E_R^1	E_R^2	E_R^1	E_R^2

C=X	**O**	2.09	0.51	2.94	1.56
	S	2.86	1.55	3.38	2.14
	Se	3.02	1.80	3.47	2.28
	NH	1.52	0.02	2.34	1.10
	PH	2.06	0.87	2.33	1.47
	CH_2	0.85	-0.42	1.71	0.55
	SiH_2	1.99	1.51	1.94	1.87
	$C(CN)_2$	2.86	2.21	3.48	2.45
α	**N**	2.37	0.70	3.53	2.16
	B	2.13	0.69	2.65	-0.03
	P	2.41	0.89	3.29	2.06
	Si	2.08	0.70	2.50	1.68
β	**N**	2.58	0.92	3.35	1.94
	B	1.87	0.25	2.83	1.44
	P	2.45	0.97	3.37	2.06
	Si	1.95	0.48	2.32	1.75
γ	**N**	2.58	0.92	3.35	1.94
	B	1.87	0.25	2.83	1.44
	P	2.45	0.97	3.37	2.06
	Si	1.95	0.48	2.32	1.75
δ	**N**	2.37	0.70	3.53	2.16
	B	2.13	0.69	2.65	-0.03
	P	2.41	0.89	3.29	2.06
	Si	2.08	0.70	2.50	1.68
α	**CF_3**	2.45	0.73	3.49	2.15
	CN	2.63	0.98	3.66	2.38
	OH	2.39	1.13	2.77	1.37
	NH_2	1.82	0.57	2.25	1.05
β	**CF_3**	2.57	0.95	3.46	2.11
	CN	2.71	1.13	3.53	2.16
	OH	2.00	0.42	2.85	1.53
	NH_2	1.73	0.32	2.59	1.33
γ	**CF_3**	2.57	0.95	3.46	2.11
	CN	2.71	1.13	3.53	2.16
	OH	2.00	0.42	2.85	1.53
	NH_2	1.73	0.32	2.59	1.33
δ	**CF_3**	2.45	0.73	3.49	2.15
	CN	2.63	0.98	3.66	2.38
	OH	2.39	1.13	2.77	1.37
	NH_2	1.82	0.57	2.25	1.05