SUPPORTING INFORMATION

Predicting the localized/delocalized character of mixed-valence diquinone radical anions. Towards the right answer for the right reason

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Table S1. Computed IV-CT data (excitation energies in cm^{-1} with transition dipole moments μ_t in Debye in parentheses) and ^{1}H-HFC constants a_H in G (with number of protons in parentheses) for **1**, **2** and **3a** in different environments[a]

	environment	E_1 ($\mu_{t,1}$)	E_2 ($\mu_{t,2}$)	E_3 ($\mu_{t,3}$)	a_H
1	gas phase	1924 (7.67)	3273 (0.00)	11519 (1.12)	-1.3 (4)
		[1924 (7.67)]	[3267 (0.00)]	[11515 (1.12)]	[-1.3 (4)]
	DCM	5730 (0.12)	8690 (1.31)	8820 (1.04)	-2.5 (2)
		[894 (12.73)]	[3450 (0.00)]	[11518 (1.40)]	[-1.2 (4)]
	DMF	6318 (0.11)	9379 (1.33)	10106 (0.93)	-2.5 (2)
		[879 (12.85)]	[3490 (0.00)]	[11538 (1.39)]	[-1.2 (4)]
2	gas phase	8225 (6.47)	16192 (0.00)	24205 (0.00)	-0.8 (4), 1.8 (2)
		[8226 (6.47)]	[16192 (0.00)]	[21310 (0.00)]	[-0.8 (4), 1.8 (2)]
	DCM	7495 (7.74)	16216 (0.00)	21847 (0.03)	-0.7 (4), 1.8 (2)
		[7494 (7.74)]	[16220 (0.00)]	[21844 (0.03)]	[-0.7 (4), 1.8 (2)]
	DMF	7547 (7.72)	16222 (0.03)	21908 (0.03)	-0.7 (4), 1.8 (2)
		[7532 (7.72)]	[16226 (0.00)]	[21906 (0.03)]	[-0.7 (4), 1.8 (2)]
	DMSO	7577 (7.68)	16225 (0.04)	21911 (0.03)	-0.7 (4), 1.8 (2)
		[7561 (7.69)]	[16230 (0.00)]	[21909 (0.03)]	[-0.7 (4), 1.8 (2)]
3a	gas phase	5135 (11.22)	5399 (0.00)	12817 (0.10)	-1.4 (4), 1.3 (2), 1.0 (4)
		[5137 (11.22)]	[5404 (0.00)]	[12830 (0.10)]	[-1.4 (4), 1.3 (2), 1.0 (4)]
	DCM	7645 (1.32)	8258 (6.63)	13499 (0.40)	-3.5 (2), -0.2 (2), 0.4 (4)
		[3767 (15.28)]	[6490 (0.00)]	[13183 (0.06)]	[-1.4 (4), 1.5 (2), 1.0 (4)]
	DMF	8033 (1.38)	9246 (6.00)	13702 (0.52)	-3.6 (2), -0.3 (2), 0.3 (4)
		[3780 (15.29)]	[6642 (0.00)]	[13228 (0.04)]	[-1.4 (4), 1.5 (2), 1.0 (4)]

[a] BLYP35/TZVP/CPCM results; values in brackets are at the symmetrical transition-state structure.

Table S2. Computed IV-CT data (excitation energies in cm^{-1} with transition dipole moments μ_t in Debye in parentheses) and ^{1}H-HFC constants a_H in G (with number of protons in parentheses) for **3b** and **4** in different environments[a]

	env.	E_1 ($\mu_{t,1}$)	E_2 ($\mu_{t,2}$)	E_3 ($\mu_{t,3}$)	a_H
3b	gas phase	4862 (0.00)	5136 (12.11)	12848 (0.08)	1.2 (8), 1.3 (2), 1.0 (4)
		[4862 (0.00)]	[5136 (12.11)]	[12847 (0.08)]	[1.2 (8), 1.3 (2), 1.0 (4)]
	THF	6776 (1.25)	7982 (7.49)	13378 (0.29)	4.1 (2), 3.3 (2), 0.4 (4), -0.2 (2)
		[3864 (15.90)]	[5559 (0.00]	[13168 (0.04)]	[1.1 (8), 1.4 (2), 1.0 (4)]
	DCM	6866 (1.25)	8206 (7.34)	13378 (0.32)	4.1 (2), 3.4 (2), 0.4 (4), -0.2 (2)
		[5013 (0.00)]	[5110 (12.10)]	[12751 (0.10)]	[1.2 (8), 1.3 (2), 1.0 (4)]
	DMF	7198 (1.32)	9262 (6.65)	13503 (0.41)	4.3 (2), 3.4 (2), 0.3 (2),-0.3 (2) 0.4 (2)
		[3824 (16.06)]	[5679 (0.00)]	[13217 (0.04)]	[1.1 (8), 1.3 (2), 1.0 (4)]
	MeCN	7208 (1.26)	9295 (6.50)	13503 (0.39)	4.3 (2), 3.4 (2), 0.3 (2),-0.3 (2) 0.4 (2)
		[4078 (15.28)]	[5689 (0.00)]	[13217 (0.04)]	[1.1 (8), 1.3 (2), 1.0 (4)]
4	gas phase	2946 (5.24)	15107 (0.25)	19357 (0.03)	-1.0 (4), 0.1 (4)
		[2942 (5.24)]	[15097 (0.25)]	[19352 (0.03)]	[-1.0 (4), 0.1 (4)]
	DCM	6600 (1.53)	13891 (0.03)	19527 (0.15)	-2.2 (2), 0.1 (2)
		[2072 (7.17)]	[14321 (0.17)]	[18239 (0.00)]	[-0.9 (4), 0.1 (4)]
	DMF	7399 (1.38)	14043 (0.03)	19615 (0.04)	-2.3 (2), 0.1 (2)
		[2082 (7.18)]	[14213 (0.15)]	[18137 (0.00)]	[-0.9 (4), 0.1 (4)]
	MeCN	7394 (1.36)	14041 (0.03)	19616 (0.04)	-2.3 (2), 0.1 (2)
		[2257 (6.79)]	[14215 (0.15)]	[18149 (0.00)]	[-0.9 (4), 0.1 (4)]
	DMSO	7459 (1.37)	14043 (0.04)	19602 (0.04)	-2.3 (2), 0.1 (2)
		[2110 (7.12)]	[14206 (0.15)]	[18132 (0.00)]	[-0.9 (4), 0.1 (4)]

[a] BLYP35/TZVP/CPCM results; values in brackets are at the symmetrical transition-state structure.

Table S3. Dependence of computed[a] ground state dipole moments μ (in Debye), ET barriers $\Delta H^{\ddagger}$ (in kJ mol^{-1}), C-O bond lengths (d_1, d_2 in Å), IV-CT excitation energies (E_1 and $2H_{ab}$ in cm^{-1})[b] for **2** on exchange-correlation functional

functional	environment	μ	$\Delta H^{\ddagger}$	d_1(C-O)	d_2(C-O)	E_1	$2H_{ab}$	μ_t (E_1)	μ_t ($2H_{ab}$)
BMK	gas phase	0.01	0.1	1.228	1.228	7978	7983	6.72	6.72
	DCM	0.57	0.0	1.230	1.232	7193	7174	8.06	8.07
	DMF	3.45	0.1	1.224	1.239	7795	7211	7.49	8.06
	DMSO	3.57	0.2	1.224	1.240	7863	7241	7.42	8.02
M05-2X	gas phase	0.00	0.0	1.231	1.231	7617	7624	7.15	7.14
	DCM	5.64	1.3	1.221	1.249	9444	6656	6.58	8.67
	DMF	6.30	2.0	1.221	1.251	10152	6694	6.22	8.65
	DMSO	6.34	2.1	1.221	1.251	10217	6729	6.18	8.60
LC-ωPBE	gas phase	0.50	0.0	1.228	1.231	7292	7261	7.92	7.94
	DCM	7.61	6.0	1.216	1.251	13617	5965	5.55	9.87
	DMF	8.04	7.2	1.216	1.252	14352	6009	5.35	9.84
	DMSO	8.06	7.3	1.216	1.252	14413	6055	5.32	9.78

[a] Gaussian 09 results. Cf. Table 1 and Table S1 for BLYP35 and experimental data. [b] Excitation energies E_1 at symmetry-broken minimum and $2H_{ab}$ at symmetrical transition state structure.

Table S4. Dependence of computed[a] ground state dipole moments μ (in Debye), ET barriers $\Delta H^{\ddagger}$ (in kJ mol^{-1}), C-O bond lengths (d_1, d_2 in Å), excitation energies (E_1 and $2H_{ab}$ in cm^{-1})[b] for **3a** on exchange-correlation functional

functional	environment	μ	$\Delta H^{\ddagger}$	d_1(C-O)	d_2(C-O)	E_1	$2H_{ab}$	μ_t (E_1)	μ_t ($2H_{ab}$)
BMK	gas phase	0.02	-0.1	1.228	1.229	4653	4652	12.08	12.08
	DCM	17.10	12.1	1.216	1.250	8354	2930	1.41	17.67
	DMF	17.97	14.8	1.215	1.251	8876	2939	1.48	17.68
M05-2X	gas phase	10.05	1.8	1.220	1.246	5692	3587	9.32	14.66
	DCM	17.66	20.9	1.218	1.256	9729	-[c]	1.61	26.63
	DMF	18.40	23.8	1.218	1.257	10138	-[c]	1.64	26.97
LC-ωPBE	gas phase	14.08	20.5	1.214	1.247	5288	-[c]	1.52	15.51
	DCM	19.10	45.3	1.214	1.253	6142	-[c]	1.73	14.70
	DMF	19.72	48.6	1.215	1.254	6211	-[c]	1.71	14.74

[a] Gaussian 09 results. Cf. Table 1 and Table S1 for BLYP35 and experimental data. [b] Excitation energies E_1 at symmetry-broken minimum and $2H_{ab}$ at symmetrical transition state structure. [c] Negative excitation energies due to triplet-instability of the ground state at the saddle point; cf. main text.

Table S5. Dependence of computed[a] ground state dipole moments μ (in Debye), ET barriers $\Delta H^{\ddagger}$ (in kJ mol^{-1}), C-O bond lengths (d_1, d_2 in Å), excitation energies (E_1 and $2H_{ab}$ in cm^{-1})[b] for **3b** on exchange-correlation functional

functional	environment	μ	$\Delta H^{\ddagger}$	d_1(C-O)	d_2(C-O)	E_1	$2H_{ab}$	μ_t (E_1)	μ_t ($2H_{ab}$)
BMK	gas phase	28.08	0.0	1.230	1.231	4154	4158	0.00	0.00
	DCM	44.88	10.3	1.217	1.252	7233	3021	1.30	18.41
	DMF	45.73	12.7	1.217	1.253	7690	3028	1.37	18.42
	MeCN	45.72	12.7	1.217	1.253	7701	3354	1.32	17.20
M05-2X	gas phase	38.54	3.1	1.221	1.249	5443	3571	0.86	15.76
	DCM	45.67	19.0	1.219	1.259	8935	-[c]	1.52	28.06
	DMF	46.34	21.7	1.219	1.260	9311	-[c]	1.56	28.30
	MeCN	46.33	21.7	1.219	1.260	9325	581	1.50	43.54
LC-ωPBE	gas phase	42.43	15.0	1.215	1.250	4551	-[c]	1.57	19.80
	DCM	47.06	38.3	1.215	1.256	5441	-[c]	1.89	16.09
	DMF	47.59	42.8	1.215	1.257	5631	-[c]	1.85	16.17
	MeCN	47.58	42.8	1.215	1.257	5652	-[c]	1.77	16.34

[a] Gaussian 09 results. Cf. Table 1 and Table S2 for BLYP35 and experimental data. [b] Excitation energies E_1 at symmetry-broken minimum and $2H_{ab}$ at symmetrical transition state structure. [c] Negative excitation energies due to triplet-instability of the ground state at the saddle point; cf. main text.

Table S6. Dependence of computed[a] ground state dipole moments μ (in Debye), ET barriers $\Delta H^{\ddagger}$ (in kJ mol^{-1}), C-O bond lengths (d_1, d_2 in Å), excitation energies (E_1 and $2H_{ab}$ in cm^{-1})[b] for **4** on exchange-correlation functional

functional	environment	μ	$\Delta H^{\ddagger}$	d_1(C-O)	d_2(C-O)	E_1	$2H_{ab}$	μ_t (E_1)	μ_t ($2H_{ab}$)
BMK	gas phase	4.62	0.0	1.228	1.228	2689	2688	5.54	5.54
	DCM	11.07	15.5	1.212	1.254	7765	1673	1.31	8.16
	DMF	11.42	17.7	1.212	1.255	8570	1690	1.21	8.16
	MeCN	11.41	17.7	1.212	1.255	8565	1911	1.19	7.56
	DMSO	11.44	17.9	1.212	1.255	8624	1726	1.20	8.06
M05-2X	gas phase	8.41	6.6	1.213	1.253	4700	1762	2.02	7.04
	DCM	11.09	25.5	1.214	1.260	11447	-[c]	1.03	8.89
	DMF	11.42	27.8	1.215	1.261	12256	-[c]	0.99	8.92
	MeCN	11.42	27.8	1.215	1.261	12248	-[c]	0.97	9.92
	DMSO	11.45	27.9	1.214	1.261	12304	-[c]	0.98	9.04
LC-ωPBE	gas phase	8.73	28.2	1.211	1.252	12737	-[c]	0.97	5.97
	DCM	11.17	48.0	1.212	1.258	15721	-[c]	0.06	5.89
	DMF	11.49	50.3	1.212	1.258	15831	-[c]	0.06	5.90
	MeCN	11.49	50.2	1.212	1.258	15829	-[c]	0.06	5.90
	DMSO	11.51	50.4	1.212	1.258	15837	-[c]	0.06	5.90

[a] Gaussian 09 results. Cf. Table 1 and Table S2 for BLYP35 and experimental data. [b] Excitation energies E_1 at symmetry-broken minimum and $2H_{ab}$ at symmetrical transition state structure. [c] Negative excitation energies due to triplet-instability of the ground state at the saddle point; cf. main text.

Table S7. Calculated properties (dipole moments μ in Debye, ET barriers $\Delta H^{\ddagger}$ in kJ mol^{-1}, C-O distances d_1 and d_2 of the both quinones in Å, excitation energies E_1 and $2H_{ab}$ in cm^{-1}, and corresponding transition dipole moments μ_t in Debye) for **1**, dependent on solvent model[a]

environment	solvent model	μ	$\Delta H^{\ddagger}$	d_1(C-O)	d_2(C-O)	E_1	$2H_{ab}$[b]	μ_t (C_1)	μ_t (C_i)
gas phase	-	0.05	0.0	1.230	1.230	1923	1922	7.67	7.67
hexane	COSMO	0.54	0.0	1.231	1.232	1365	1363	9.85	9.85
MeCN	COSMO	18.45	30.3	1.214	1.259	6407	1384	0.10	9.81
DMF	COSMO	18.45	30.3	1.214	1.259	6407	1384	0.10	9.81
	D-COSMO-RS	18.79	28.5	1.214	1.256	6997	1393	0.10	9.84

[a] TURBOMOLE 6.3 BLYP35/TZVP results. [b] Excitation energy at the symmetrical transition state structure.

Table S8. Calculated properties (dipole moments μ in Debye, ET barriers $\Delta H^{\ddagger}$ in kJ mol^{-1}, C-O distances d_1 and d_2 of the both quinones in Å, excitation energies E_1 and $2H_{ab}$ in cm^{-1}, and corresponding transition dipole moments μ_t in Debye) for **2**, dependent on solvent model[a]

environment	solvent model	μ	$\Delta H^{\ddagger}$	d_1(C-O)	d_2(C-O)	E_1	$2H_{ab}$[b]	μ_t (C_1)	μ_t (C_2)
EtOAc	COSMO	0.70	0.1	1.234	1.238	7946	7928	7.17	7.19
	D-COSMO-RS	0.61	0.1	1.234	1.237	7897	7881	7.19	7.20
EtOAc – *t*-BuOH (10:1)	COSMO	0.90	0.1	1.234	1.239	7967	7940	7.15	7.18
DCM	COSMO	0.92	0.1	1.234	1.239	8009	7976	7.13	7.16
	D-COSMO-RS	1.45	0.0	1.234	1.241	8074	8012	7.08	7.15
DMF	COSMO	3.11	0.2	1.230	1.245	8364	8057	6.80	7.12

[a] TURBOMOLE 6.3 BLYP35/TZVP results. [b] Excitation energy at the symmetrical transition state structure.

Table S9. Calculated properties (dipole moments μ in Debye, ET barriers $\Delta H^{\ddagger}$ in kJ mol^{-1}, C-O distances d_1 and d_2 of the both quinones in Å, excitation energies E_1 and $2H_{ab}$ in cm^{-1}, and corresponding transition dipole moments μ_t in Debye) for **3a**, dependent on solvent model[a]

environment	solvent model	μ	$\Delta H^{\ddagger}$	d_1(C-O)	d_2(C-O)	E_1	$2H_{ab}$[b]	μ_t (C_1)	μ_t (C_i)
EtOAc	COSMO	0.04	0.0	1.239	1.239	4460	4454	13.33	13.33
	D-COSMO-RS	0.21	0.1	1.238	1.238	4424	4416	13.37	13.38
EtOAc – *t*-BuOH	COSMO	0.05	0.0	1.239	1.239	4470	4464	13.32	13.32
(10:1)	D-COSMO-RS	16.46	10.0	1.221	1.258	8084	4463	1.24	13.33
t-BuOH	COSMO	16.48	9.6	1.222	1.257	8142	4512	1.23	13.26
	D-COSMO-RS	18.38	17.7	1.221	1.267	9199	4708	1.31	13.01

[a] TURBOMOLE 6.3 BLYP35/TZVP results. [b] Excitation energy at the symmetrical transition state structure.

Table S10. Calculated properties (dipole moments μ in Debye, ET barriers $\Delta H^{\ddagger}$ in kJ mol^{-1}, C-O distances d_1 and d_2 of the both quinones in Å, excitation energies E_1 and $2H_{ab}$ in cm^{-1}, and corresponding transition dipole moments μ_t in Debye) for **3b**, dependent on solvent model[a]

environment	solvent model	μ	$\Delta H^{\ddagger}$	d_1(C-O)	d_2(C-O)	E_1	$2H_{ab}$[b]	μ_t (C_1)	μ_t (C_i)
gas phase	-	0.14	0.0	1.235	1.235	4865	5133	0.01	12.12
DCM	COSMO	15.78	6.9	1.223	1.259	6979	4494	1.12	14.11
	D-COSMO-RS	15.53	6.6	1.224	1.260	7145	4522	1.11	14.05
t-BuOH	COSMO	16.32	8.1	1.223	1.260	7185	4511	1.15	14.08
DMF	COSMO	17.21	10.3	1.223	1.261	7539	4542	1.21	14.03

[a] TURBOMOLE 6.3 BLYP35/TZVP results. [b] Excitation energy at the symmetrical transition state structure.

Table S11. Calculated properties (dipole moments μ in Debye, ET barriers $\Delta H^{\ddagger}$ in kJ mol^{-1}, C-O distances d_1 and d_2 of the both quinones in Å, excitation energies E_1 and $2H_{ab}$ in cm-1, and corresponding transition dipole moments μ_t in Debye) for **4**, dependent on solvent model[a]

environment	solvent model	μ	$\Delta H^{\ddagger}$	d_1(C-O)	d_2(C-O)	E_1	$2H_{ab}$[b]	μ_t (C_1)	μ_t (C_2)
EtOAc	COSMO	10.66	11.9	1.216	1.260	6175	2410	1.54	6.29
	D-COSMO-RS	10.62	10.6	1.217	1.258	5798	2432	1.66	6.30
EtOAc – *t*-BuOH	COSMO	10.74	12.5	1.216	1.260	6361	2412	1.49	6.28
(10:1)	D-COSMO-RS	11.06	16.1	1.216	1.262	7630	2427	1.24	6.29
DCM	COSMO	10.94	14.1	1.217	1.261	6886	2450	1.39	6.27
	D-COSMO-RS	10.93	13.9	1.217	1.262	6867	2442	1.38	6.26
t-BuOH	COSMO	11.14	15.4	1.217	1.261	7324	2463	1.31	6.27
	D-COSMO-RS	11.76	26.5	1.216	1.268	10468	2439	0.91	6.24
MeCN	COSMO	11.47	17.8	1.217	1.262	8122	2474	1.19	6.26
	D-COSMO-RS	11.34	15.5	1.217	1.260	7438	2494	1.31	6.28
DMF	COSMO	11.47	17.8	1.217	1.262	8123	2474	1.19	6.26
	D-COSMO-RS	11.48	15.4	1.217	1.259	7323	2503	1.34	6.28

[a] TURBOMOLE 6.3 BLYP35/TZVP results. [b] Excitation energy at the symmetrical transition state structure.